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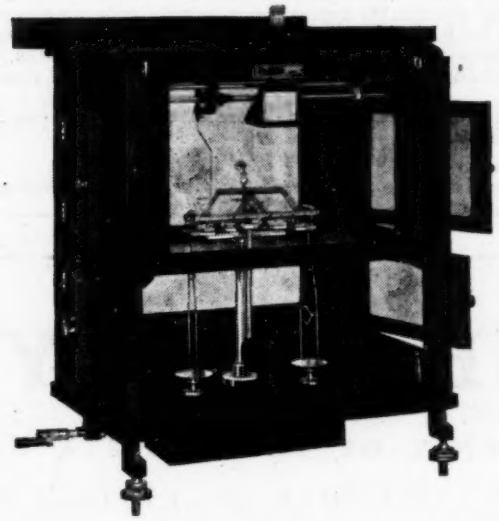

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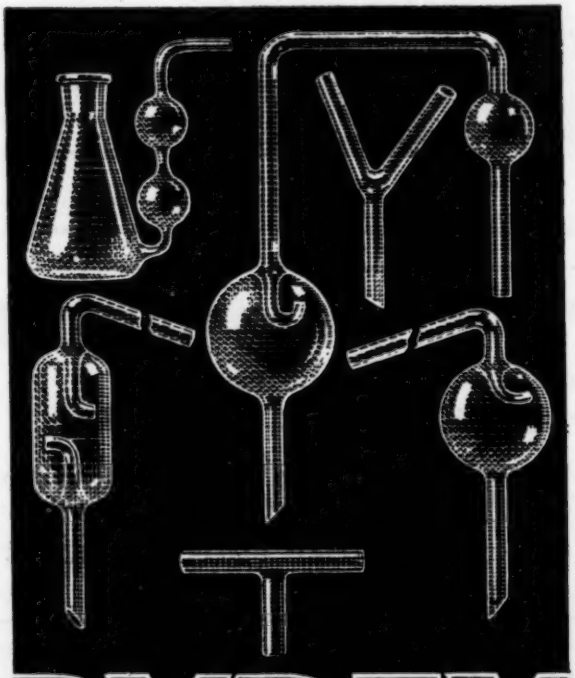

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General, Physical, and Inorganic.

PAGE

123. The Kinetics of the Reaction between Copper and Iodine in Aqueous (Potassium Iodide) Solution. Part I.
By L. Leighton Bircumshaw and Maurice H. Everdell 598

132. Some Further Observations on the Interchange of Heavy Oxygen between Water and Certain Inorganic Oxy-anions.
By E. R. S. Winter and H. V. A. Briscoe 631

134. The Crystal Structure of Phosphorus Pentachloride.
By D. Clark and H. M. Powell and (independently) A. F. Wells 642

Organic.

119. The Condensation of Some Aromatic Ketones with Ethyl Succinate.
By C. L. Hewett 585

120. The Active Principles of Leguminous Fish-poison Plants. Part VII. The Reduction of Elliptone.
By Stanley H. Harper 587

121. The Active Principles of Leguminous Fish-poison Plants. Part VIII. The Synthesis of Dehydrotetrahydroelliptone and of Dehydrotetrahydromalaccol.
By Stanley H. Harper 593

122. The Active Principles of Leguminous Fish-poison Plants. Part IX. The Synthesis of Furano-*iso*flavones related to Rotenone.
By Stanley H. Harper 595

124. Alkyl–Oxygen Fission in Carboxylic Esters. Part II. Derivatives of *p*-Methoxybenzhydrol.
By Michael P. Balfe, Mark A. Doughty, Joseph Kenyon, and Reginald Poplett . 605

125. The Separation of Diastereoisomerides by Selective Adsorption on Optically Inactive Material.
By Margaret M. Jamison and E. E. Turner 611

126. The Mechanism of Additions to Double Bonds. Part XIV. The Nature of the Activated Complex in Bimolecular Diene Syntheses.
By Albert Wassermann 612

127. Homogeneous Catalysis of Diene Syntheses. A New Type of Third-order Reaction.
By Albert Wassermann 618

128. Solvent Effects in Association Equilibria.
By Albert Wassermann 621

129. Homogeneous Catalysis and Solvent Effects in a Diene Synthesis.
By Albert Wassermann 623

130. Indeno-2″ : 3″ : 2′ : 1′-benzanthrone.
By G. Swain and A. R. Todd 626

131. *Cannabis Indica*. Part XI. An Examination of the Alkali-soluble Portion of American Hemp Resin.
By (Mrs.) A. Madinaveitia, P. B. Russell, and A. R. Todd 628

133. The Associating Effect of the Hydrogen Atom. Part XI. Hydrogen Bonds involving the Sulphur Atom. The S–H–N Bond.
By Gordon Hopkins and Louis Hunter 638

Obituary 646

INDEX OF AUTHORS' NAMES.

Balfe, M. P., Doughty, M. A., Kenyon, J., and Poplett, R., 605.
Bircumshaw, L. L., and Everdell, M. H., 598.
Briscoe, H. V. A. See Winter, E. R. S.
Clark, D., Powell, H. M., and Wells, A. F., 642.
Doughty, M. A. See Balfe, M. P.
Everdell, M. H. See Bircumshaw, L. L.
Harper, S. H., 587, 593, 595.
Hewett, C. L., 585.
Hopkins, G., and Hunter, L., 638.
Hunter, L. See Hopkins, G.
Jamison, M. M., and Turner, E. E., 611.
Kenyon, J. See Balfe, M. P.
Madinaveitia, (Mrs.) A., Russell, P. B., and Todd, A. R., 628.
Poplett, R. See Balfe, M. P.
Powell, H. M. See Clark, D.
Russell, P. B. See Madinaveitia, (Mrs.) A.
Swain, G., and Todd, A. R., 626.
Todd, A. R. See Madinaveitia, (Mrs.) A., and Swain, G.
Turner, E. E. See Jamison, M. M.
Wassermann, A., 612, 618, 621, 623.
Wells, A. F. See Clark, D.
Winter, E. R. S., and Briscoe, H. V. A., 631.

In all cases, addition of sodium nitrite accelerated the reactions, and with acid of *d* 1·12 it produced a little *N*-nitroso-*p*-nitromethylaniline, while diminishing the yield of 3 : 3′ : 5 : 5′-tetranitrotetramethylbenzidine from *ca.* 40% to *ca.* 2·5%. With nitric acid of *d* 1·12 at 50°, only *ca.* 2·0% of the last-named compound was formed, almost pure 2 : 4-dinitrodimethylaniline being the main product in contrast to the much more contaminated product formed at 0°. Urea almost inhibited the reaction in acid of *d* 1·12 and delayed considerably the reactions in the more concentrated acids.

Nitric acid, *d* 1·42, expelled the methyl groups from 3 : 3′ : 5 : 5′-tetranitrodimethylbenzidine; the product crystallised rapidly from hot nitrobenzene in bright yellow, lenticular plates or slowly in rhomboidal plates, m. p. 227° (decomp.) (van Romburgh, *Rec. Trav. chim.*, 1886, **5**, 240, describes the compound as exploding above 220°) (Found : N, 23·4. Calc. : N, 23·2%). This behaviour is parallel with that of nitric acid on dimethylaniline, and on 2 : 4-dinitrodimethylaniline, both of which formed 2 : 4 : 6-trinitromethylaniline with acid of *d* 1·42 and *N* : 2 : 4 : 6-tetranitromethylaniline with acid of *d* 1·5.

p-Nitrosodimethylaniline, dissolved in acid of *d* 1·42, gave 2 : 4-dinitrodimethylaniline at 0° and 2 : 4-dinitromethylaniline when the temperature was allowed to rise.

The authors thank Imperial Chemical Industries (Dyestuffs) Ltd. for gifts of chemicals.—Technical College, Huddersfield. [*Received, May 20th*, 1942.]

Preparation of 1 : 2 : 4 : 5-*Tetraphenylbenzene from Benzylideneacetophenone.* By Alexander Schönberg and Abdel Fattah Aly Ismail.

Straus and Ehrenstein (*Annalen*, 1925, **442**, 105) showed that benzylideneacetophenone, when treated with phosphorus pentachloride, yielded the abnormal ketochloride αγ-dichloro-αγ-diphenylpropylene (I) (compare also Straus, *ibid.*, 1912, **393**, 238). The same substance was prepared more conveniently by means of oxalyl chloride (Staudinger, *Ber.*, 1909, **42**, 3975).

Straus and Ehrenstein (*loc. cit.*), by the action of phenylmagnesium bromide on (I), obtained a small amount of a substance, m. p. 152—154° (decomp.), believed to be αζ-dichloro-αγδζ-tetraphenyl-$\Delta^{\alpha\epsilon}$-hexadiene (III), as a by-product.

We treated (I) in dry acetone with potassium iodide; iodine was liberated and from the product (III) was obtained in good yield. This process proceeds probably in two stages: (1) one chlorine atom in (I), which is very reactive, is replaced by iodine with the formation of (II); (2) iodine is liberated and the two residues unite with the formation of (III). This reaction is similar to the formation of ethyl ethylenetetracarboxylate from ethyl dibromomalonate by means of sodium iodide (Finkelstein, *Ber.*, 1910, **43**, 1528).

When (III) is heated above its m. p., hydrogen chloride is evolved and 1 : 2 : 4 : 5-tetraphenylbenzene (V) formed almost quantitatively. It is assumed that (III) tautomerises to (IV), from which two molecules of hydrogen chloride are easily liberated. Substances (II) and (IV) are hypothetical intermediates. 1 : 2 : 4 : 5-Tetraphenylbenzene is thus now easily available.

$$2CHPh{:}CH{\cdot}COPh \xrightarrow{(COCl)_2} 2CHPhCl{\cdot}CH{:}CPhCl \xrightarrow{KI} [2CHPhI{\cdot}CH{:}CPhCl]$$
(I) (II.)

$$\xrightarrow{-I_2} \begin{matrix}CHPh{\cdot}CH{:}CPhCl\\ CHPh{\cdot}CH{:}CPhCl\end{matrix} \longrightarrow \left[\begin{matrix}CPh{:}CH{\cdot}CHPhCl\\ CPh{:}CH{\cdot}CHPhCl\end{matrix}\right] \xrightarrow{-2HCl} \begin{matrix}CPh{:}CH{\cdot}CPh\\ CPh{:}CH{\cdot}CPh.\end{matrix}$$
(III.) (IV.) (V.)

αζ-Dichloro-αγδζ-tetraphenyl-$\Delta^{\alpha\epsilon}$*-hexadiene* (III).—Benzylideneacetophenone (5 g.) was refluxed with oxalyl chloride (3·6 g.) for 10 hours (calcium chloride guard-tube) (Staudinger, *loc. cit.*), the excess of oxalyl chloride driven off, and the product (I) dissolved in acetone (50 c.c., free from water and alcohol). On addition of potassium iodide (9 g.) iodine was almost immediately liberated. After 7 hours' refluxing, the mixture was cooled in ice, and the precipitate (III) collected and washed with sulphurous acid. A further quantity was obtained from the acetone filtrate by concentration and cooling or by pouring in sulphurous acid and cooling. The precipitate separated from acetone, acetone–methyl alcohol, or chloroform–methyl alcohol (charcoal) in colourless crystals, m. p. 159—160° (decomp. and formation of a red liquid) (Found : C, 79·1; H, 5·3. Calc. for $C_{30}H_{24}Cl_2$: C, 79·1; H, 5·3%).

1 : 2 : 4 : 5-*Tetraphenylbenzene* (V).—1 G. of (III) was heated at about 200° (bath temp.) for 1 hour with occasional stirring, hydrogen chloride being evolved. The product separated from benzene–light petroleum (b. p. 70—80°) in long colourless needles, m. p. 264° (sublimation), not depressed by authentic 1 : 2 : 4 : 5-tetraphenylbenzene (Durand and Hsun, *Compt. rend.*, 1930, **191**, 1461; cf. Dilthey and Hurtig, *Ber.*, 1934, **67**, 2004) (Found : C, 94·4; H, 5·6. Calc. for $C_{30}H_{22}$: C, 94·3; H, 5·7%). The yield was almost quantitative.—Fouad I University, Cairo, Egypt. [*Received, April 24th*, 1942.]

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119. *The Condensation of Some Aromatic Ketones with Ethyl Succinate.*

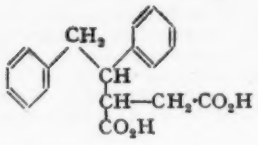
By C. L. Hewett.

Deoxybenzoin, 2-benzoylnaphthalene, and 6-benzoyltetralin have been condensed with ethyl succinate. The acid arising from deoxybenzoin has been reduced and the two *acids* thus obtained have been cyclised to the two stereoisomeric 3 : 10-*diketo*-3 : 4 : 9 : 10 : 11 : 12-*hexahydro*-1 : 2-*benzanthracenes* (II). 2-Benzoylnaphthalene gave *γ-phenyl-γ-naphthylitaconic acid*, which was reduced to the corresponding *methylsuccinic acid*. 6-Benzoyltetralin gave a mixture of two *acids*, both of which were resistant to reduction.

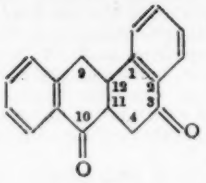
By the condensation of ethyl succinate with deoxybenzoin, Stobbe and Russwarm (*Annalen*, 1899, **308**, 157) obtained γ-phenyl-γ-benzylidenemethylsuccinic acid, but they made no attempt to reduce this to γ-phenyl-γ-benzylmethylsuccinic acid (I).

In the hope that the acid (I) could be obtained from the unsaturated acid by reduction and subsequently cyclised to 3 : 10-diketo-3 : 4 : 9 : 10 : 11 : 12-hexahydro-1 : 2-benzanthracene (II), thus providing a new route to derivatives of 1 : 2-benzanthracene, the reduction of this acid was investigated. Reduction with sodium amalgam yielded a mixture of two *acids*, of which the less soluble one (m. p. 188—189°) was isolated in a state of purity; the second *acid* was obtained from the liquors and had m. p. 122·5—123·5°, raised to 138° after

drying at 100°/0·5 mm. This acid was probably still contaminated with unsaturated acid (see below). Cyclisation of both acids gave a mixture of two neutral products, m. p. 210—211° and 132—133°, which are



(I.)



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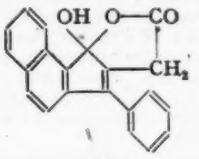
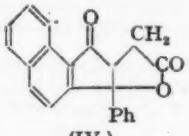


(III.)

regarded as the *diketones* (II). The higher-melting isomer was also obtained from the lower-melting isomer in an attempted Clemmensen reduction.

In a dissertation (Frankfurt-am-Main; 1937) * Knott has also described the reduction of γ-phenyl-γ-benzylidenemethylsuccinic acid and the ring closure of the reduced acid. He describes two reduced acids, m. p. 193° and 155°. The latter acid was obtained pure by hydrolysis of its anhydride. The two higher-melting acids would appear to be the same; the discrepancy between the m. p.'s of the two lower-melting acids may be due to contamination of the acid described in this paper with the unsaturated acid. On ring closure of his two acids, Knott obtained only the higher-melting neutral product from his higher-melting acid; from the lower-melting acid he obtained the same product together with another neutral product, m. p. 142·5°. Both of these compounds he formulates as the keto-enol, since they give monodinitrophenylhydrazones and monoximes.



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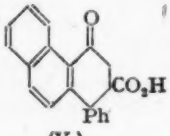

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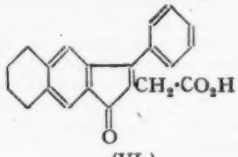

(VI.)

The condensation of 2-benzoylnaphthalene with ethyl succinate gave a good yield of a single *acid*, which cyclised with sulphuric acid to give a neutral product, probably the *lactone* (III) or (IV). Reduction of the unsaturated acid was effected with sodium amalgam, which was slow in action. Ring closure of the anhydride of the reduced acid gave the *keto-acid* (V).

6-Benzoyltetralin condensed with ethyl succinate to give a mixture of two unsaturated *acids* which were both resistant to reduction with sodium amalgam. One of the unsaturated acids on cyclisation with sulphuric acid gave a *keto-acid*, probably the indone (VI).

Owing to present circumstances, it is not possible to continue this investigation.

Experimental.

γ-Phenyl-γ-benzylmethylsuccinic Acid (I).—γ-Phenyl-γ-benzylidenemethylsuccinic acid (41 g.) (Stobbe and Russwarm, *loc. cit.*) was dissolved in water (500 c.c.) and sodium hydroxide (8·2 g.) and treated with sodium amalgam (2½%; 400 g.). After the sodium had all reacted the solution was decanted and acidified. The precipitated oil slowly set to a paste and was triturated with acetic acid, and the solid recrystallised from acetic acid. *γ-Phenyl-γ-benzylmethylsuccinic acid* (5 g.) separated in colourless needles, m. p. 188—189° (Found: C, 72·1; H, 5·9. $C_{18}H_{18}O_4$ requires C, 72·5; H, 6·1%). The mother-liquors on dilution with water gave a product, m. p. 83—95°, which after recrystallisation from benzene formed colourless needles, m. p. 122·5—123·5°. This isomeric *γ-phenyl-γ-benzylmethylsuccinic acid* after drying at 100°/0·5 mm. had m. p. 138° (Found: C, 73·1; H, 5·9%).

3 : 10-*Diketo*-3 : 4 : 9 : 10 : 11 : 12-*hexahydro*-1 : 2-*benzanthracene* (II).—The higher-melting acid (5 g.) was dissolved in concentrated sulphuric acid (25 c.c.) and heated on the water-bath for 1 minute, cooled, and poured on ice. The product was extracted with ether, filtered from a sparingly soluble crystalline solid, and the ethereal solution, after washing with sodium carbonate solution, dried and evaporated. The residue was dissolved in hot methyl alcohol, filtered from a further amount of sparingly soluble crystals, and allowed to crystallise. The *diketone* (II, probably the *cis*-isomer) separated in colourless plates (0·2 g.), m. p. 132—133° (Found: C, 82·6; H, 5·9. $C_{18}H_{14}O_2$ requires C, 82·4; H, 5·4%). The sparingly soluble fractions were boiled with dilute sodium carbonate solution, washed with water, and crystallised from benzene; the other isomer (probably *trans*) of the *diketone* then separated in colourless plates (0·5 g.), m. p. 210—211° (Found: C, 82·2; H, 5·4%). Cyclisation of the lower-melting acid (10 g.) with concentrated sulphuric acid (25 c.c.) on the water-bath for 2 minutes gave the higher-melting ketone (0·1 g.), m. p. 209—210°, but the product was mainly the lower-melting isomer (3·3 g.), m. p. 132—133°.

The lower-melting diketone (1·8 g.) was boiled with amalgamated zinc (6 g.), water (8 c.c.), concentrated hydrochloric acid (4 c.c.), and toluene (2·5 c.c.) for 5 hours. The product on crystallisation from benzene had m. p. 209—210°, not depressed by the higher-melting diketone.

γ-Phenyl-γ-naphthylitaconic Acid.—2-Benzoylnaphthalene (105 g.), prepared by dehydrogenation of 6-benzoyltetralin with sulphur (Scharwin, *Ber.*, 1902, **35**, 2513; Barbot, *Bull. Soc. chim.*, 1930, **47**, 1318), and ethyl succinate (105 g.) were added to a suspension of sodium ethoxide (prepared from 21 g. of sodium, 42 g. of ethyl alcohol, and 200 c.c. of ether) and heated on the water-bath for 1 hour. Water (500 c.c.) was then added, and the aqueous layer separated; hydrolysis was completed by boiling the aqueous layer with sodium hydroxide (50 g.). After acidification the crude acid was dissolved in sodium carbonate solution and filtered (charcoal), and the sodium salt salted out. The acid obtained by

* A copy of this dissertation was sent to Professor J. W. Cook after the experiments now recorded had been completed.

decomposition of the sodium salt was dissolved in benzene; after 1 day *γ-phenyl-γ-naphthylitaconic acid* (97 g.) separated, which after crystallisation from benzene–toluene formed colourless micro-crystals, m. p. 173·5—174·5° (Found: C, 75·5; H, 5·0. $C_{21}H_{16}O_4$ requires C, 75·9; H, 4·85%). It separated from aqueous acetic acid in colourless plates, m. p. 154—158°. The *dimethyl* ester prepared from the acid and diazomethane, separated from methyl alcohol in colourless plates, m. p. 94—95° (Found: C, 76·2; H, 5·75. $C_{23}H_{20}O_4$ requires C, 76·65; H, 5·6%).

Cyclisation. The foregoing acid (5 g.) was dissolved in concentrated sulphuric acid (50 c.c.) and after 20 minutes at the ordinary temperature was poured on ice. The solid *lactone* (III or IV) was collected, washed free from colouring matter with sodium carbonate solution, and crystallised from a large amount of methyl alcohol, forming colourless needles (1·5 g.), m. p. 166·5—167·5° (Found: C, 79·7; H, 4·6. $C_{21}H_{14}O_3$ requires C, 80·2; H, 4·5%). Its formulation as a lactone is based on the fact that it is insoluble in sodium carbonate solution, but slowly dissolves in boiling alcoholic sodium hydroxide, from which it is precipitated by acids but not by water.

γ-Phenyl-γ-naphthylmethylsuccinic Acid.—The foregoing acid (45 g.) was dissolved in water (450 c.c.) and sodium hydroxide (11·7 g.) and treated with sodium amalgam (2½%; 900 g.) on a water-bath. After all the sodium had reacted the solution was decanted, filtered (charcoal), and sodium chloride added. The sodium salt which separated was decomposed with dilute hydrochloric acid, and the free acid extracted with ether. After removal of the ether the residue was crystallised from acetic acid (charcoal) and then benzene–light petroleum; the *acid* (35 g.) then separated as a snow-white powder, m. p. 130—131° (Found: C, 75·15; H, 5·7. $C_{21}H_{18}O_4$ requires C, 75·4; H, 5·4%).

4-Keto-1-phenyl-1 : 2 : 3 : 4-tetrahydro-2-phenanthroic Acid (V).—The reduced acid (35 g.) was refluxed with acetyl chloride (35 g.) and after removal of the acetic acid and excess of acetyl chloride the crude anhydride was dissolved in nitrobenzene (350 c.c.). Aluminium chloride (35 g.) was added with ice-cooling and after 20 hours at 0° the product was decomposed with ice, and the nitrobenzene distilled with steam. The residue was extracted with sodium carbonate solution, filtered, and acidified; the resulting *keto-acid* (16·3 g.) crystallised from acetic acid in colourless needles, m. p. 243—245° after sintering at 240° (Found: C, 79·25; H, 5·3. $C_{21}H_{16}O_3$ requires C, 79·7; H, 5·1%). It was converted into a gum on attempted Clemmensen reduction.

γ-Phenyl-γ-(6-tetralyl)itaconic Acid.—6-Benzoyltetralin (Scharwin, *loc. cit.*) (90 g.), ethyl succinate (90 g.), and ether (90 c.c.) were added to sodium ethoxide (prepared from 18 g. of sodium, 36 g. of ethyl alcohol, and 180 c.c. of ether), and the whole heated on the water-bath for 2½ hours, the alcohol and ether being allowed to distil off. Water (500 c.c.) and sodium hydroxide (50 g.) were then added, and the solution boiled for 1½ hours and acidified. The precipitated oil was dissolved in water (500 c.c.) and potassium hydroxide (60 g.) and boiled for a further 8 hours. The hot solution was saturated with potassium carbonate, and the potassium salt which separated on cooling crystallised from water and decomposed with dilute acid; the pure *acid* (30 g.) crystallised from acetic acid in fine colourless plates, m. p. 183—185° (Found: C, 74·6; H, 6·0. $C_{21}H_{20}O_4$ requires C, 74·95; H, 6·0%). The liquors of the potassium salt were acidified, and the sticky acid extracted with benzene. After standing for several days at 0° a new *acid* (43 g.) separated, which after recrystallisation from toluene formed a colourless microcrystalline powder, m. p. 188—189° (Found: C, 75·4; H, 6·2%). A mixture of the two acids had m. p. 169—175°.

Cyclisation. A solution of the acid, m. p. 183—185° (5 g.), in concentrated sulphuric acid (25 c.c.) was stirred for 1 minute at the ordinary temperature and then poured on ice. The solid was collected, reprecipitated from its filtered solution in sodium carbonate solution, and crystallised from acetic acid. The *keto-acid* (2·4 g.) formed red needles, m. p. 165—166° (Found: C, 79·0; H, 5·7. $C_{21}H_{16}O_3$ requires C, 79·2; H, 5·7%). From its colour and by analogy with the cyclisation of other diarylitaconic acids (Stobbe and Vieweg, *Ber.*, 1902, **35**, 637) this compound is probably the indone (VI).

Reduction. In a typical experiment, the acid, m. p. 188—189° (45 g.), was dissolved in water (400 c.c.) and sodium hydroxide (9·6 g.), and sodium amalgam (2½%; 600 g.) added. After heating on the water-bath for 4 hours and standing at the ordinary temperature for 20 hours, the solution was filtered (charcoal) and acidified. The oily acid was extracted with ether, the ether evaporated, and the residue crystallised from benzene. The product had m. p. 100—160°, indicating that some reduction had taken place.

The author thanks the British Empire Cancer Campaign for a grant to the Hospital which has assisted this investigation.

THE CHESTER BEATTY RESEARCH INSTITUTE, THE ROYAL CANCER HOSPITAL (FREE), LONDON, S.W.3. [*Received, May 22nd,* 1942.]

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120. *The Active Principles of Leguminous Fish-poison Plants. Part VII. The Reduction of Elliptone.*

By STANLEY H. HARPER.

The course of the reduction of *l*- and *dl*-elliptones in acetic acid over platinum oxide catalyst has been elucidated, and the following stages characterised: dihydroelliptone, dihydrodeoxyelliptone, octahydrodeoxyelliptone, and perhydroelliptone.

The zinc–alkali reduction of the dehydro-compounds has been shown to give, in addition to acids of the derrisic acid type, phenols analogous to derritol.

Oxidation of elliptone with nitrous acid has given elliptonone, a diketone, whose structure has been established by a partial synthesis from elliptol, the phenol obtained in the zinc–alkali reduction of dehydroelliptone.

Biological trials using the chrysanthemum aphis as test insect have shown that *l*-elliptone is, next to rotenone, the most toxic insecticidal substance to be isolated from *Derris* resin in an optically active form. In the order of decreasing toxicity: *l*-elliptone > *dl*-elliptone > *l*-dihydroelliptone > *dl*-dihydroelliptone.

l-DIHYDROROTENONE has gained some prominence in recent years in the United States as a substitute for rotenone in insecticide sprays. This use appears to be based on two considerations, first, its stability, and secondly its high toxicity. Jones *et al.* (*J. Econ. Entomol.*, 1933, **26**, 451) have shown that *l*-dihydrorotenone is more resistant to atmospheric oxidation and is at least as toxic as rotenone to culicine mosquito larvæ. More recently Sullivan *et al.* (*Soap*, 1939, **15**, No. 7, 107) have shown that *l*-dihydrorotenone is only slightly less toxic than rotenone to the housefly (*Musca domestica* L.). Biological trials on *l*-elliptone have shown that it is the next most toxic optically active substance to rotenone to be isolated from *Derris* resin (this paper and see also

(I.)
(II.)
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(VIII.)
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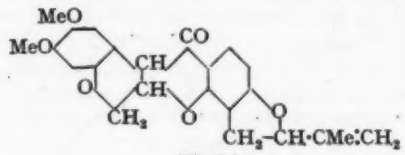
(XI.)
(XII.)
(XIII.)
(XIV.)
(XV.)

Martin, *Ann. Appl. Biol.*, **1942**, **29**, 75). For this reason the preparation of optically active and inactive dihydroelliptones was considered of interest so that their relative toxicities to elliptone and rotenone could be determined. In view also of conflicting statements in the literature, the reduction of elliptone under various conditions has been examined in some detail.



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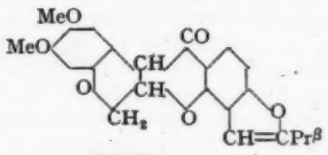

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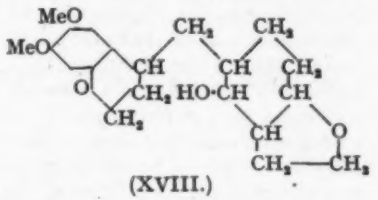

(XVIII.)

The exocyclic double bond of rotenone (XVI) can be hydrogenated under very mild conditions and, by suitable choice of solvent and catalyst, with the virtual absence of other hydrogenation products (Haller and Schaffer, *Ind. Eng. Chem.*, **1933**, **25**, 983). Elliptone (I), with its cyclic double bond, is, however, analogous to *iso*rotenone (XVII), which is known to be difficult to reduce. LaForge and Smith (*J. Amer. Chem. Soc.*, **1929**, **51**, 2574) were unable to reduce *iso*rotenone, but Butenandt and Hildebrandt (*Annalen*, **1930**, **477**, 261) effected reduction over platinum-black in acetic acid to give a product which they did not characterise. Re-examination of this (see p. 593) has shown it to be impure *l*-dihydrodeoxy*iso*rotenone and there was no evidence of the formation of *l*-dihydro*iso*rotenone. Hence the use of more active catalysts for the reduction of elliptone would at the same time facilitate the formation of by-products.

The reduction of elliptone by means of platinum oxide in ethyl acetate with fission of the furan ring to give tetrahydroelliptone (III) has already been described by the author (J., 1939, 1099). The only other reduction recorded is that by Meijer and Koolhaas (*Rec. Trav. chim.*, 1939, **58**, 875), in which elliptone (described there as derride) was hydrogenated in acetic acid in the presence of platinum oxide. About 5 molecules of hydrogen were absorbed, and a crystalline product isolated, to which the formula $C_{20}H_{26}O_5$ was given. It was stated to be insoluble in aqueous sodium hydroxide but gave a brown colour with ferric chloride, and was formulated as (XVIII). This formula, however, requires $C_{20}H_{28}O_5$ and is not consistent with the ferric chloride colour.

The hydrogenation of elliptone in acetic acid has therefore been examined. The initial absorption of hydrogen was fairly rapid, with a break between 1 and 2 molecules, after which hydrogenation proceeded slowly until the hydrogenation curve was asymptotic to an absorption of 10 molecules of hydrogen. This corresponds to the reduction of the keto-group, the furan ring, and both aromatic rings. The reaction mixture gave a small yield of a neutral crystalline substance, $C_{20}H_{26}O_5$, and with the same melting point as the substance described by Meijer and Koolhaas (*loc. cit.*). Although they are considered to be identical, this substance gave no colour with ferric chloride and was recovered unchanged from attempted acetylation and oximation. It therefore contains neither a keto-group nor hydroxyl-groups. It was optically active, so C_7–C_8, the seat of asymmetry in the molecule, was unchanged, *i.e.*, ring C could not have suffered fission (cf. the rotenols, in which C_7–C_8 is inactive). The substance is therefore considered to be *octahydrodeoxyelliptone* (XV). The non-crystalline portion of the reduction product is probably a mixture of stereoisomeric perhydroelliptones.

To obtain *l*-dihydroelliptone experiments were made, the reduction being stopped when one molecule of hydrogen had been absorbed. Products were obtained, however, that varied in melting point and optical rotation and no homogeneous product could be obtained. It was evident that the reduction was not wholly stepwise, *i.e.*, some reduction of the dihydroelliptone was taking place while elliptone remained unreduced. By stopping the reaction at 2 molecules absorption, this was overcome, and l-*dihydroelliptone* (II) was obtained in good yield, its high specific rotation in benzene providing a ready check on its purity. That it was the true dihydro-compound and not a deoxyelliptone was established by characterisation of the keto-group through an *oxime*, an enolic *acetate*, and oxidation with iodine to a dehydro-compound. In all hydrogenations in acetic acid over platinum oxide there was little if any fission of the furan ring to tetrahydroelliptone (III), in marked contrast to reduction in ethyl acetate over the same catalyst, in which reduction appears to proceed directly to the ring-open tetrahydro-product (J., 1939, 1099). dl-*Dihydroelliptone* was obtained (1) by reduction of *dl*-elliptone under the above conditions, and (2) by racemisation of *l*-dihydroelliptone with sodium acetate in alcohol, the products being identical. This method of racemising C_7–C_8 has already been used for the preparation of *dl*-elliptone (*loc. cit.*). The same dehydro-compound, *dehydrodihydroelliptone* (V), was obtained by oxidation of both *l*- and *dl*-dihydroelliptones with iodine.

In one reduction of *dl*-elliptone in acetic acid the experiment was stopped when 2·5 molecules of hydrogen had been absorbed. Crystallisation failed to give a homogeneous product, but by making use of the sparing solubility of the benzene *solvate* of *dl*-dihydroelliptone a more soluble constituent was isolated in about 10% yield. Analysis showed this to be dl-*dihydrodeoxyelliptone* (XIV). In the light of this, the substance previously described as *l*-dihydroelliptone (J., 1939, 1099) was re-examined. Fresh analyses supported the formula $C_{20}H_{20}O_5$ and it was not oximated under conditions which sufficed for *l*-dihydroelliptone. There is little doubt that it is impure l-*dihydrodeoxyelliptone*. Butenandt (*Annalen*, 1928, **494**, 266) has recorded the formation of dihydrodeoxyrotenone in the reduction of rotenone when carried to 3 molecules absorption under similar conditions. It is evident that the reduction of elliptone over platinum in acetic acid proceeds through the

following stages: elliptone (I) ⟶ dihydroelliptone (II) ⟶ dihydrodeoxyelliptone (XIV) ⟶ octahydrodeoxyelliptone (XV) ⟶ perhydroelliptone.

The zinc–alkali reduction of dehydroelliptone (IV) was used previously (J., 1939, 1424) for the preparation of elliptic acid (VII). It was observed at that time that the crude acid had m. p. 140—145° and needed repeated crystallisation for purification (m. p. 190°). Fractional crystallisation later showed that a second phenolic constituent was present and the method has therefore been modified to enable the phenol, *elliptol*, to be separated chemically. From its formula, $C_{18}H_{16}O_6$, insolubility in sodium bicarbonate, and solubility in potassium hydroxide solution this substance is analogous to derritol. Hence it is ascribed the structure (X), this being confirmed by the formation of a *monomethyl* ether with methyl sulphate and alkali. This ether was exactly analogous to derritol methyl ether in being insoluble in potassium hydroxide solution but still giving a ferric chloride colour. The di-*o*-substituted hydroxyl group has therefore remained unmethylated, as would be expected under such conditions. In like manner dehydrodihydroelliptone gave *dihydroelliptic acid* (VIII), also obtained by the hydrogenation of elliptic acid over platinum oxide in dioxan, and *dihydroelliptol* (XI). *Dehydrotetrahydroelliptone* (VI), obtained from *l*- or *dl*-tetrahydroelliptone by oxidation with iodine and also by the hydrogenation of dehydroelliptone over platinum oxide in ethyl acetate, gave on zinc–alkali reduction *tetrahydroelliptic acid* (IX) and *tetrahydroelliptol* (XII). The formation of elliptol was unexpected, as no parallel formation of derritol in the zinc–alkali reduction of dehydrorotenone had been reported. Nevertheless the repetition of this reaction with dehydrorotenone led in one experiment to a good yield of derritol. A number of experiments have been made, both the time and the method of addition of the reagents being varied, but so far with no clue as to the factors governing the formation of derritol and of elliptol in this reaction.

Meijer and Koolhaas (*loc. cit.*) by the chromic acid oxidation of elliptone obtained a diketone, derridenone, $C_{20}H_{12}O_7$, analogous to rotenonone. The same diketone, for which the name elliptonone is preferred, has now been obtained by treatment of elliptone with nitrous acid (cf. dihydrorotenone ⟶ dihydrorotenononone; LaForge and Smith, *J. Amer. Chem. Soc.*, 1930, **52**, 1091). The structure (XIII) assigned to it by Meijer and Koolhaas has been confirmed by a partial synthesis from elliptol. Elliptol readily condensed with a molecule of methyl oxalate in the presence of sodium acetate to give elliptonone in good yield (cf. the synthesis of rotenonone from derritol; Takei, *Ber.*, 1932, **65**, 1041).

TABLE I.

Test Insect: *Macrosiphoniella sanborni* Gill (Chrysanthemum aphis) (viviparous parthogenetic females).
Carrying Medium: 0·1% sulphonated lorol + 10% acetone.
The pressure and the gap at the bottom of the spray tower were adjusted to give a deposit of approximately 500 mg. on a 9 cm. Petri dish. Temp. 68° F. Rel. humidity 58%. Sprayed in triplicate, fifteen insects per dish.

Substance.	Concn., mg./l.	% Kill.	Substance.	Concn., mg./l.	% Kill.	Substance.	Concn., mg./l.	% Kill.
l-Elliptone	20	96	*l*-Dihydroelliptone	40	38	Rotenone	4	100
	10	84		20	40		2	89
	5	36		10	33		1	18
dl-Elliptone	20	89	*dl*-Dihydroelliptone	40	39		0·5	11
	10	70		20	16	Control	—	4
	5	9		10	4			

With the co-operation of Dr. C. Potter some of the substances described in this paper have been compared with rotenone for their relative toxicities as insecticides. The general technique has been described by Potter (*Ann. Appl. Biol.*, 1941, **28**, 142). From the percentage kills *l*-elliptone is approximately one-fifth as toxic as rotenone, a result closely in accord with the more accurate figure published by Martin (*ibid.*, 1942, **29**, 75) for a comparison using the same insect but in an alcohol–saponin medium. This potency of *l*-elliptone places the compound second in importance to rotenone among the optically active principles so far separated from *Derris* resin.

The remaining substances tested can qualitatively be placed in the following order of decreasing toxicity: *l*-Elliptone > *dl*-Elliptone > *l*-Dihydroelliptone > *dl*-Dihydroelliptone. In marked contrast to *l*-dihydrorotenone, *l*-dihydroelliptone is distinctly much less toxic than *l*-elliptone. Further the optically active forms are distinctly more toxic than the corresponding racemic forms of each pair of compounds tested, a conclusion in agreement with other workers' observations in this series of compounds. Fink and Haller (*J. Econ. Ent.*, 1936, **29**, 594) have observed that *l*-> *dl*-*iso*rotenone and *l*-> *dl*-dihydrodeguelin to culicine mosquito larvæ. Sullivan *et al.* (*loc. cit.*) have also observed that *l*-> *dl*-dihydrodeguelin to the housefly. Tattersfield and Martin (*Ann. Appl. Biol.*, 1938, **25**, 411) have shown that *l*-> *dl*-toxicarol to the bean aphis.

EXPERIMENTAL.

Before analysis all substances in this and the following two papers were dried for 1 hour at 100° in a high vacuum. Microanalyses are by Drs. Weiler and Strauss, Oxford. Methoxyl determinations are by the author, using Clark's semi-micro-method (*J. Assoc. Off. Agric. Chem.*, 1932, **15**, 136). Melting points were observed in Mason's apparatus (*Chem. and Ind.*, 1925, 577), soft glass tubes being used, and are uncorrected.

Under the same conditions that rotenone forms a 1 : 1 solvate with dichloroacetic acid [Jones, *Ind. Eng. Chem.* (*Anal.*), 1938, **10**, 684] *l*-elliptone forms a similar *solvate*, crystallising in needles, m. p. 108° (67·1 mg. required 6·90 c.c. of 0·02N-potassium hydroxide. Calc. for $C_{20}H_{16}O_6,CHCl_2{\cdot}CO_2H$: 6·96 c.c.). If present, therefore, in crude rotenone, elliptone would interfere in the estimation of the purity of the latter by this proposed volumetric method. *dl*-Elliptone

does not, however, form a solvate with dichloroacetic acid. Neither *l*- nor *dl*-elliptone forms a solvate with carbon tetrachloride, though both are only sparingly soluble in that solvent.

Relative Stability of Rotenone and Elliptone.—100 Mg. of each in acetone (25 c.c.) were aerated side by side in bright sunlight intermittently for several days. At 4 hours the rotenone solution was yellow. After 12 hours, when the elliptone solution was still colourless, the solutions were evaporated. The rotenone gave a non-crystalline red gum, but the elliptone was recovered in crystalline form with unchanged m. p. Acetone was used as the solvent because Jones (*Ind. Eng. Chem.*, 1931, **23**, 387) has shown that, of the solvents he examined, rotenone was least decomposed in acetone on aeration in sunlight.

Relative Goodhue Values.—*l*- and *dl*-Elliptones gave the Goodhue test (*J. Assoc. Off. Agric. Chem.*, 1936, **19**, 118) with equal intensity, but more strongly than rotenone.

l-Elliptone exhibits dimorphism on crystallisation from alcohol; when first isolated (*Chem. and Ind.*, 1939, **58**, 292) it had m. p. 159° but subsequent preparations have had a higher m. p. 171—172° but with unchanged specific rotation (J., 1941, 878). The influence of the type of glass used for the m. p. determinations has recently been reported (*loc. cit.*).

Isolation of dl-*Elliptone and* dl-*Deguelin from* D. malaccensis (cf. J., 1940, 1182).—The alkali-washed neutral resin (100 g.) from 4 kg. of " Kinta type " root was dissolved in carbon tetrachloride (250 c.c.) and seeded with rotenone complex. On refrigeration rotenone–carbon tetrachloride solvate (20 g.) separated. The soluble resin was recovered by evaporation and dissolved in ether (500 c.c.). A crop (9 g.) slowly separated which by fractional crystallisation gave small quantities of *dl*-elliptone, m. p. 183°, not depressing the m. p. of an authentic specimen (Found : OMe, 17·5. Calc. for $C_{20}H_{16}O_6$: OMe, 17·6%), and of *dl*-deguelin, m. p. 174°, not depressing the m. p. of an authentic specimen (Found : OMe, 15·9. Calc. for $C_{23}H_{22}O_6$: OMe, 15·7%). From this it is concluded that *l*-elliptone and *l*-deguelin were present in the original resin, but were racemised during the alkali treatment and the prolonged crystallisation. The bulk of the crystalline material could not be separated into any chemical entities and without doubt contained dehydro-compounds formed by aerial oxidation during the crystallisation.

The technique for the isolation of *l*-elliptone described previously (J., 1939, 1102), being utilised, *l*-elliptone has been isolated (0·5% calc., on root) from *D. elliptica* (Changi type) (ethyl acetate extract 27%, rotenone 9%) and from further specimens of *D. elliptica* (var. Sarawak creeping). Elliptone could not be isolated from a sample of cube of unknown origin (ethereal extract 14%), but no opportunity has occurred of examining an authentic specimen of *Lonchocarpus utilis*.

Fractionation of Elliptone-free D. elliptica *Resin.*—The ethereal solution from 5 kg. of *D. elliptica* root from which *l*-elliptone no longer crystallised (for details, see J., 1939, 1102) was washed with 5% potassium hydroxide solution, dilute acid, and water, and the neutral resin obtained by evaporation. This resin (216 g.) was dissolved in benzene (500 c.c.) and precipitated with successive portions of light petroleum (b. p. 40—60°, 2 × 750 c.c.). The first precipitate (123 g.) was redissolved in benzene (350 c.c.), and divided into two fractions by light petroleum (450 c.c.). The following fractions were obtained in order of increasing solubility :

			$[\alpha]_D^{19°}$ in benzene (c = 4).	OMe, %.
Ppte. A.	Sticky red resin	26 g.	−32°	13·7
Ppte. B.	Hard red resin	81 g.	−53	15·4
Ppte. C.	Hard red resin	58 g.	−56	15·9
Soln. D.	Yellow opaque wax	51 g.	−48	11·5

Fraction B in ether gave a small yield of *dl*-elliptone (1·02 g.) after prolonged refrigeration, but no further crystals. Fraction D on treatment with light petroleum gave a soluble fraction nearly free from rotenoids (OMe, 4·2%. Durham test, very faint). No crystalline material could be obtained from any of the other fractions. These results closely parallel those obtained with a column of activated alumina by which *dl*-elliptone was first isolated (Harper, *Chem. and Ind.*, 1938, **57**, 1059).

Reduction of l-*Elliptone in Acetic Acid* (cf. Meijer and Koolhaas, *Rec. Trav. chim.*, 1939, **58**, 878).—*l*-Elliptone (1 g.) in " AnalaR " acetic acid (20 c.c.) was reduced in the presence of platinum oxide (100 mg.). After absorption of 2 mols. of hydrogen reduction was slow, the final absorption being 9·7 mols. after 100 hours, which corresponds to complete reduction of the keto-group and of the aromatic rings. The solution was filtered and poured into water, and the product taken out in ether. The extract was washed with 5% potassium hydroxide solution (nothing soluble), and the neutral gum recovered. In contact with methyl alcohol part crystallised, and was recrystallised from that solvent to give *octahydrodeoxyelliptone* (XV) (160 mg.), m. p. 160° (Found : C, 69·2; H, 7·5. $C_{20}H_{24}O_6$ requires C, 69·3; H, 7·5%). $[\alpha]_D^{18°}$ −10° in acetone (c = 1·0) and −8° in benzene (c = 1·0). This substance is without doubt the same as that described by Meijer and Koolhaas, and, as they found, nothing crystalline could be obtained from the alcoholic filtrate, the gum probably consisting of a mixture of stereoisomeric perhydroelliptones.

In another experiment octahydrodeoxyelliptone was isolated in what is presumably a dimorphic form, m. p. 139°, $[\alpha]_D^{17°}$ −8° in benzene (c = 1·0) (Found : C, 69·5; H, 7·6%).

By interrupting the reduction when 2 mols. of hydrogen had been absorbed it was possible to obtain optically pure l-*dihydroelliptone* (II) in good yield. It crystallised from alcohol in needles, m. p. 191°, $[\alpha]_D^{19°}$ −132° in benzene (c = 1·0) (Found : C, 67·7; H, 5·1; OMe, 17·4. $C_{20}H_{18}O_6$ requires C, 67·8; H, 5·1; 2OMe, 17·5%).

The *oxime*, prepared as described for elliptone β-oxime (J., 1939, 1103), had m. p. 250° (Found : N, 3·9. $C_{20}H_{19}O_6N$ requires N, 3·8%). The *monoacetate*, prepared as described for elliptone (*loc. cit.*), had m. p. 208° (Found : C, 66·6; H, 5·1; OMe, 15·7. $C_{22}H_{20}O_7$ requires C, 66·6; H, 5·1; 2OMe, 15·7%).

Reduction of dl-*Elliptone in Acetic Acid.*—dl-*Dihydroelliptone* (II), crystallising from alcohol in prisms, m. p. 188°, was obtained in good yield by the reduction of *dl*-elliptone in acetic acid following the conditions outlined for *l*-dihydroelliptone above (Found : C, 67·2; H, 5·1; OMe, 17·8%). From benzene, in which it was sparingly soluble, *dl*-dihydroelliptone separated as a *solvate* (cf. *dl*-elliptone, *loc. cit.*), in hard prisms, m. p. 188° (Found : OMe, 15·5. $2C_{20}H_{18}O_6.C_6H_6$ requires OMe, 15·7%).

In one reduction of *dl*-elliptone in acetic acid in the presence of platinum oxide, slightly more than 2 mols. of hydrogen were absorbed before the reduction was interrupted. Repeated crystallisation failed to yield a homogeneous product of sharp m. p. Separation was eventually effected by means of cold benzene, in which the solvate of *dl*-dihydroelliptone remained undissolved. Crystallisation from alcohol of the material soluble in benzene gave dl-*dihydrodeoxyelliptone* (XIV) in fine plates, m. p. 157—159° (Found : C, 70·6; H, 6·0; OMe, 18·3. $C_{20}H_{22}O_5$ requires C, 70·6; H, 5·9; 2OMe, 18·2%), in about 10% yield.

Re-examination of the substance reported previously as *l*-dihydroelliptone (J., 1939, 1104), m. p. 159°, $[\alpha]_D^{20°}$ −97° in acetone (c = 1·0), has shown it to be impure l-*dihydrodeoxyelliptone* (Found : C, 70·2; H, 5·5; OMe, 18·1%). After recovery from an attempted oximation in sodium acetate–alcohol the substance had m. p. 170° (Found : C, 70·0; H, 5·9%); perhaps it was purer *l*-dihydrodeoxyelliptone, but insufficient material has prevented elucidation of this point.

Racemisation of l-*Dihydroelliptone.*—*l*-Dihydroelliptone (250 mg.) and sodium acetate (500 mg.) in alcohol (20 c.c.) were refluxed for 2 hours. On cooling, *dl*-dihydroelliptone separated and was recrystallised from alcohol, m. p. 188°,

$[\alpha]_D$ $\pm 0°$ in chloroform (130 mg.), identical with that obtained by the reduction of *dl*-elliptone (cf. the racemisation of *l*-elliptone, *loc. cit.*).

Dehydrodihydroelliptone (V).—To *l*- or *dl*-dihydroelliptones (250 mg.) and sodium acetate (500 mg.) in boiling alcohol (20 c.c.), iodine (500 mg.) in alcohol (5 c.c.) was added slowly, and refluxing continued for 3 hours, during which time the *dehydro*-compound crystallised. It was recrystallised from chloroform–alcohol, separating in bright yellow plates (133 mg.), m. p. 264° (Found: C, 68·0; H, 4·6; OMe, 17·6. $C_{20}H_{16}O_6$ requires C, 68·2; H, 4·6; 2OMe, 17·6%). It was an apparently dimorphic form of that obtained by cyclisation of dihydroelliptic acid (see below).

Action of Zinc and Alkali on Dehydroelliptone.—Dehydroelliptone (1·5 g.), zinc dust (5 g.), and 15% aqueous potassium hydroxide (10 c.c.) in ethyl alcohol (30 c.c.) were refluxed for 2 hours. The filtered liquid was acidified (hydrochloric acid) and diluted till crystallisation commenced. The whole was extracted with ether, and the ethereal suspension shaken with saturated sodium bicarbonate solution. The aqueous layer containing suspended sodium elliptate was filtered. Solution of the sparingly soluble sodium salt in boiling water and acidification gave pure elliptic acid (VII) (750 mg.), m. p. 190°. The sodium bicarbonate filtrate was acidified to give elliptic acid (370 mg.) that required recrystallisation before purity was attained. Esterification with alcoholic sulphuric acid and recrystallisation from ethyl alcohol gave *ethyl elliptate*, m. p. 142°, in microcrystalline needles [Found: OMe, 22·1. $C_{22}H_{22}O_6$ requires 2OMe + OEt (calc. as 3OMe), 22·3%]. This ester gave a slight depression of m. p. (to 130—135°) with methyl elliptate (J., 1939, 1426) of the same m. p.

The ethereal layer was evaporated, and the gum crystallised from aqueous methyl alcohol to give *elliptol* (X) in narrow plates, m. p. 163° (Found: C, 65·6; H, 4·9; OMe, 18·9. $C_{18}H_{16}O_6$ requires C, 65·8; H, 4·9; 2OMe, 18·9%). It gave a deep blue ferric chloride colour.

Elliptol (100 mg.), dissolved in 2% potassium hydroxide solution (2 c.c.), was shaken with methyl sulphate (0·1 c.c.). Next day the precipitate was collected and crystallised from methyl alcohol to give *elliptol methyl ether* (78 mg.), m. p. 137° (Found: OMe, 26·7. $C_{19}H_{18}O_6$ requires 3OMe, 27·1%).

Following these observations the action of zinc and alkali on dehydrorotenone has been re-examined. In one experiment under the above conditions derritol was isolated in good yield (14·5 g. from 50 g. of dehydrorotenone). In another experiment in which the acidified alcoholic filtrate was concentrated before ether extraction, the main product from the ethereal layer was a substance, m. p. 95°, insoluble in 5% potassium hydroxide solution but giving a violet ferric chloride colour. Comparison with a sample prepared by direct esterification of derrisic acid with alcoholic sulphuric acid showed this substance to be ethyl derrisate [Found: OMe, 20·1. Calc. for $C_{25}H_{28}O_8$: 2OMe + OEt (as 3OMe), 20·3%].

Cyclisation of Elliptic Acid.—Elliptic acid (1 g.) and sodium acetate (500 mg.) in acetic anhydride (10 c.c.) and acetic acid (1 c.c.) were refluxed for 5 mins., then diluted with alcohol (40 c.c.) and left overnight. The yellow needles (120 mg.) were collected and recrystallised from chloroform–alcohol to give dehydroelliptone (IV), m. p. 262—264°, identical with an authentic specimen (J., 1939, 1103). The alcoholic filtrate was evaporated, and the gum rubbed with sodium carbonate solution. Acidification of the filtrate gave impure acetylelliptic acid (45 mg.), m. p. 120°, which could not be purified. Crystallisation from alcohol of the portion insoluble in sodium carbonate gave *ethyl acetylelliptate* (224 mg.), m. p. 151—153° [Found: C, 62·5; H, 5·0; OMe, 19·1. $C_{24}H_{24}O_9$ requires C, 63·1; H, 5·3; 2OMe + OEt (as 3OMe), 20·4%]. This ester was insoluble in 5% potassium hydroxide solution, and like the crude acid, gave no colour with ferric chloride.

Reduction of Elliptic Acid.—Elliptic acid (3·5 g.) in dioxan (100 c.c.) was shaken with hydrogen in the presence of platinum oxide (0·5 g.). After 12 hours (absorption 400 c.c., including that of the catalyst) the reaction mixture was filtered and evaporated. The residue, sparingly soluble in alcohol or ethyl acetate, crystallised in hard irregular tablets (2·2 g.), m. p. 200°. Analysis showed it to be *dihydroelliptic acid* (VIII) (Found: C, 61·7; H, 5·2; OMe, 15·7. $C_{20}H_{20}O_6$ requires C, 61·8; H, 5·2; 2OMe, 15·9%). With alcoholic ferric chloride it gave a wine-red colour. The acid gave no depression of m. p. with elliptic acid. Its identity as dihydroelliptic acid was finally established by comparison with an authentic specimen prepared from dehydrodihydroelliptone (see below). Esterification of a suspension of the acid in benzene–ether with diazomethane gave the *methyl* ester, crystallising from alcohol in prisms, m. p. 149° (Found: OMe, 23·1. $C_{21}H_{22}O_6$ requires 3OMe, 23·1%). With alcoholic ferric chloride it gave a wine-red colour, thus distinguishing it from methyl elliptate (m. p. 143°), with which it gave no depression of m. p. Esterification with ethyl alcohol–sulphuric acid and crystallisation from ethyl alcohol gave *ethyl dihydroelliptate* in needles, m. p. 147° [Found: OMe, 22·1. $C_{22}H_{24}O_6$ requires 2OMe + OEt (as 3OMe), 22·3%].

Neither elliptic acid nor methyl elliptate could be reduced in ethyl acetate suspension in the presence of platinum oxide. Dihydroelliptic acid could not be further reduced in dioxan in the presence of platinum oxide.

Cyclisation of Dihydroelliptic Acid.—Dihydroelliptic acid (500 mg.) and sodium acetate (250 mg.) in acetic anhydride (5 c.c.) and acetic acid (0·5 c.c.) were refluxed for 15 mins. The orange solution was poured into water, and the yellow solid ground with sodium bicarbonate. The neutral insoluble portion was sparingly soluble in alcohol and crystallised in straw-coloured needles, m. p. 248—250°. This form of *dehydrodihydroelliptone* (V) would appear to be a dimorph of that described above (Found: C, 68·3; H, 4·7; OMe, 17·6. $C_{20}H_{16}O_6$ requires C, 68·2; H, 4·6; 2OMe, 17·6%). Acidification of the sodium bicarbonate filtrate gave crude acetyldihydroelliptic acid, m. p. 185—190°, which could not be effectively purified.

Action of Zinc and Alkali on Dehydrodihydroelliptone.—Following the modified conditions used for dehydroelliptone (see above), dehydrodihydroelliptone (1 g.) gave dihydroelliptic acid (275 mg.), m. p. 200°, identical with that prepared by the reduction of elliptic acid (see above), and *dihydroelliptol* (XI) (336 mg.), crystallising from alcohol in plates, m. p. 190° (Found: C, 66·0; H, 5·6; OMe, 18·9. $C_{18}H_{18}O_6$ requires C, 65·5; H, 5·5; 2OMe, 18·8%). This substance was insoluble in sodium bicarbonate solution and gave a wine-red colour with alcoholic ferric chloride.

Dehydrotetrahydroelliptone (VI).—To *l*- or *dl*-tetrahydroelliptone (*loc. cit.*) (500 mg.) and sodium acetate (500 mg.) in boiling alcohol (20 c.c.), iodine (500 mg.) in alcohol (5 c.c.) was added slowly. After 6 hours' refluxing no crystals had separated; the solution was therefore concentrated and precipitated with water. The solid, after drying in a vacuum, was refluxed in acetic acid (10 c.c.) with zinc dust (500 mg.) for 2 hours. At the end of 1 hour a further 500 mg. of zinc dust were added. The solution was filtered, and the zinc washed with hot acetic acid (2 × 5 c.c.), yellow needles separating on cooling. *Dehydrotetrahydroelliptone* (240 mg.) was recrystallised from alcohol to give pale yellow needles, m. p. 260° (decomp.) (Found: C, 67·4; H, 5·0. $C_{20}H_{18}O_6$ requires C, 67·8; H, 5·1%). The dehydro-compound gave no colour with ferric chloride but was soluble in 5% potassium hydroxide solution.

Reduction of Dehydroelliptone.—An attempt to reduce dehydroelliptone (1·3 g.) in ethyl acetate suspension in the presence of platinum oxide was partly successful. After absorption had apparently ceased, the solid was treated with 2% potassium hydroxide solution and collected. Acidification of the filtrate and crystallisation from alcohol gave dehydrotetrahydroelliptone (140 mg.), m. p. 260° (decomp.), identical with that prepared above. The main insoluble portion (1·07 g.), m. p. 264° (Found: C, 67·9; H, 4·2%), appeared to consist of a mixture of dehydro- and dehydrodihydro-elliptone. The substance gave no depression of m. p. with either of these compounds. There was no evidence of the reduction of the dehydro-linkage (cf. the reduction of dehydrorotenone to dehydrotetrahydrorotenone; Haller and LaForge, *J. Amer. Chem. Soc.*, 1931, **53**, 3426).

Action of Zinc and Alkali on Dehydrotetrahydroelliptone.—Following the modified conditions used for dehydroelliptone (see p. 592), dehydrotetrahydroelliptone (300 mg.) gave *tetrahydroelliptic acid* (IX) (130 mg.) crystallising from alcohol in prisms, m. p. 202° (Found: C, 61·1: H, 5·4; OMe, 15·9. $C_{20}H_{22}O_8$ requires C, 61·5; H, 5·6; 2OMe, 15·9%), and giving a brownish-red colour with alcoholic ferric chloride. In an attempt to prepare the methyl ester the acid (50 mg.) in benzene suspension was treated overnight at 0° with excess of diazomethane. The product crystallised from alcohol in prisms (15 mg.), m. p. 123°, and was insoluble in 5% potassium hydroxide solution. It was evidently impure *methyl ester methyl ether* of tetrahydroelliptic acid (Found: OMe, 27·4. $C_{22}H_{26}O_8$ requires 4OMe, 29·6%. $C_{21}H_{24}O_8$ requires 3OMe, 23·0%), methylation occurring at the *p*-hydroxyl group of ring D.

Crystallisation of the phenolic fraction from aqueous alcohol gave *tetrahydroelliptol* (XII) in plates (60 mg.), m. p. 225° after evolution of solvent at 135—140°, but in a bath at 200° it melted immediately with effervescence (Found: C, 64·2; H, 5·7. $C_{18}H_{20}O_8$ requires C, 65·0; H, 6·1%), *i.e.*, solvent retention.

Elliptonone (XIII) (cf. Meijer and Koolhaas, *loc. cit.*).—*l*-Elliptone (500 mg.) in acetic acid (4 c.c.) and amyl nitrite (1·7 c.c.) was cooled to 0°, and a mixture of hydrochloric acid (1 c.c.) and acetic acid (1 c.c.) added during 5 minutes. After warming to room temperature the bright yellow precipitate was collected, washed with cold acetic acid, and dried over potash pellets in a vacuum. Elliptonone crystallised from xylene in yellow prisms, m. p. 315° (Found: OMe, 17·0%); it sublimed in a high vacuum at 250° and then had m. p. 325° (Found: C, 66·1; H, 3·6; OMe, 17·1. Calc. for $C_{20}H_{12}O_7$: C, 65·9; H, 3·3; 2OMe, 17·0%).

Partial Synthesis of Elliptonone (cf. synthesis of rotenonone; Takei, *Ber.*, 1932, **65**, 1047).—Elliptol (100 mg.), methyl oxalate (100 mg.), and sodium acetate (50 mg.) were heated at 160° for 1 hour. The reaction mixture was treated with boiling methyl alcohol (2 × 5 c.c.), and the residue sublimed to give elliptonone in yellow prisms, m. p. 325°, not depressing that described above.

No crystalline products could be isolated from the Clemmensen reduction of *l*- and *dl*-elliptones and of *dl*-dihydroelliptone, under conditions similar to those in which Haller and LaForge (*J. Amer. Chem. Soc.*, 1931, **53**, 3430) reduced *iso*rotenone to deoxy*iso*rotenone.

l-Elliptone could not be reduced in dioxan with either platinum oxide or a palladium–barium sulphate catalyst, although rotenone was readily reduced in the presence of the latter catalyst to dihydrorotenone in good yield (cf. Haller and Schaffer, *J. Amer. Chem. Soc.*, 1933, **55**, 3494).

Reduction of l-iso*Rotenone in Acetic Acid* (cf. Butenandt and Hildebrandt, *Annalen*, 1930, **477**, 261).—*l-iso*Rotenone (5 g.) in "AnalaR" acetic acid (100 c.c.) was hydrogenated slowly in the presence of platinum oxide (0·5 g.). There was no break in the absorption curve at 1 or 2 molecules absorption. By interrupting the reduction at 2 molecules absorption and repeatedly crystallising the product from alcohol, the substance described by Butenandt and Hildebrandt was obtained in needles, m. p. 168°, $[\alpha]_D^{17°}$ −107° in benzene (c = 1·0), in 30% yield. Despite its apparent homogeneity this substance contained unreduced *l-iso*rotenone. Oxidation with iodine in alcoholic sodium acetate and fractional crystallisation of the product gave dehydro*iso*rotenone, m. p. 195°, not depressed by an authentic specimen. Crystallisation of the more soluble fraction gave *l-dihydrodeoxyisorotenone*, m. p. 158°, in needles from alcohol and giving no colour in the Durham test; $[\alpha]_D^{19°}$ −113° in benzene (c = 1·0) (Found: C, 71·8; H, 6·2; OMe, 16·4. $C_{23}H_{26}O_8$ requires C, 72·2; H, 6·8; OMe, 16·3%).

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121. *The Active Principles of Leguminous Fish-poison Plants. Part VIII. The Synthesis of Dehydrotetrahydroelliptone and of Dehydrotetrahydromalaccol.*

By STANLEY H. HARPER.

Condensation of methyl 2-cyanomethyl-4 : 5-dimethoxyphenoxyacetate with 2-ethylresorcinol by the Hoesch method and subsequent hydrolysis gave rise to tetrahydroelliptic acid. Cyclisation of this acid with hot acetic anhydride and sodium acetate furnished through the acetate dehydrotetrahydroelliptone, identical with that prepared from elliptone. The formula established for elliptone by degradative experiments (J., 1939, 1424) has therefore been fully substantiated.

By an analogous condensation with ethylphloroglucinol, tetrahydromalaccolic acid was prepared. This acid on cyclisation gave dehydrotetrahydromalaccol, for which an angular and a linear formula are possible. It has not proved possible, however, to compare this product with that derived from natural sources.

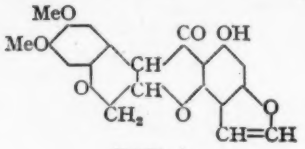
FROM the results of degradative experiments it was concluded in Part III (J., 1939, 1424) that elliptone had structure (I).* This formulation could be conclusively established by synthesis of dehydrotetrahydroelliptone (VI), a degradation product obtained recently (preceding paper). An attempt was therefore made to use the Hoesch method already successfully employed by Robertson *et al.* in the synthesis of dehydrotetrahydrorotenone (J., 1933, 1163) and of dehydrotetrahydrosumatrol (J., 1939, 1601).

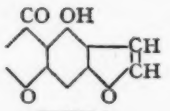
Condensation of 2-ethylresorcinol with methyl 2-cyanomethyl-4 : 5-dimethoxyphenoxyacetate by the method of Hoesch and subsequent hydrolysis of the crude ketimine gave *methyl tetrahydroelliptate*. Hydrolysis of this ester gave tetrahydroelliptic acid (IX), identical with that prepared from the reduction of elliptone (preceding paper). Cyclisation of this acid with boiling acetic anhydride and sodium acetate gave a small yield of O-*acetyldehydrotetrahydroelliptone*, which on deacetylation with hot aqueous alcoholic hydrochloric acid gave rise to dehydrotetrahydroelliptone (VI), identical with a specimen prepared from elliptone. As the cyclisation of tetrahydroelliptic acid can only occur in one direction, the structure previously assigned to elliptone and its degradation products is established conclusively.

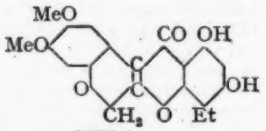
In Part IV (J., 1940, 309) an angular formula (XIX*a*) was postulated for malaccol, although the corresponding linear form (XIX*b*) could not be excluded. An attempt was therefore made to confirm this formulation by the synthesis of dehydrotetrahydromalaccol by the Hoesch method. Ethylphloroglucinol was substituted for 2-ethylresorcinol in the preceding condensation and *methyl tetrahydromalaccolate, tetrahydromalaccolic acid,*

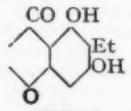
* Formulæ are numbered consecutively from the preceding paper.

O-*diacetyldehydrotetrahydromalaccol*, and *dehydrotetrahydromalaccol* were successively prepared. The last compound gave a negative Durham test and a deep green colour with ferric chloride, reactions similar to those


(XIX*a*.)


(XIX*b*.)


(XX*a*).


(XX*b*.)

of dehydromalaccol. The cyclisation of tetrahydromalaccolic acid can, however, occur in two ways to give the angular (XX*a*) or the linear (XX*b*) form of dehydrotetrahydromalaccol. There is no evidence to decide for or against either formula for this synthetic product. In the analogous case of tetrahydrosumatrolic acid Kenny, Robertson, and George (J., 1939, 1601) regarded their cyclised product as having the angular formula. It has not proved possible to prepare natural dehydrotetrahydromalaccol for comparison with this synthetic specimen. Several experiments on the oxidation of tetrahydromalaccol with iodine and subsequent reduction of the iodo-compound with zinc in acetic acid in no case led to crystalline material. Hence it has not been possible to confirm either structure postulated previously for malaccol, but the angular formula (XIX*a*) is still regarded as the more probable.

Experimental.

Veratrole.—No convenient method for the preparation of veratrole could be found in the literature. Practically no yield was obtained from pyrocatechol by the method of Perkin and Weizman (J., 1906, **89**, 1649), which may be due to the fact that the stated quantity of methyl sulphate is only one quarter of the theoretical requirement. By a modification, however, of the method for veratraldehyde (*Organic Syntheses*, **16**, 91) veratrole was prepared in 83—86% yield from both guaiacol and pyrocatechol.

Veratrole was nitrated in 100 g. lots by Clark's method (*J. Amer. Chem. Soc.*, 1931, **53**, 3434), the temperature being kept below 5° during the addition; the product, 4-nitroveratrole, without recrystallisation was suitable for reduction (97% yield, m. p. 95°). 4-Nitroveratrole was reduced to 4-aminoveratrole in 93% yield, allowing for recovered nitro-compound (Fargher, J., 1920, **117**, 869). The amine was purified by distillation, b. p. 170°/16 mm. The method of Baker and Evans for the preparation of 4-hydroxyveratrole was used (J., 1938, 375), and the yield (45%) consistently obtained. The remaining seven stages to methyl 2-cyanomethyl-4 : 5-dimethoxyphenoxyacetate were covered by the methods of Robertson *et al.* (J., 1930, 2440; 1932, 1386; 1933, 1164).

2-Ethylresorcinol was prepared substantially as described by Russell, Frye, and Mauldin (*J., Amer. Chem., Soc.*, 1940, **62**, 1442). The high yield, however, recorded by these authors in the preparation of 7-hydroxy-4-methylcoumarin could not be duplicated (yield, 60%).

Methyl Tetrahydroelliptate.—Through methyl 2-cyanomethyl-4 : 5-dimethoxyphenoxyacetate (2 g.), 2-ethylresorcinol (2 g.), and zinc chloride (2 g., fused and powdered) in dry ether (50 c.c.), dry hydrogen chloride was passed until the reactants had dissolved (1 hour), the whole being cooled in ice and salt. On keeping at 0° a brown oil separated which slowly crystallised. After 7 days the ether was decanted, and the solid washed with ether (3 × 50 c.c.) and hydrolysed by heating on the steam-bath with water (100 c.c.) for 2 hours. The precipitate was collected and stirred with sodium bicarbonate solution. After drying, the insoluble portion (1·78 g.) was repeatedly crystallised from methyl alcohol to give *methyl tetrahydroelliptate* in feathery needles, m. p. 185° (Found : C, 61·8; H, 5·75; OMe, 22·4. $C_{21}H_{24}O_8$ requires C, 62·35; H, 5·95; 3OMe, 23·0%). The ester gave a red colour with alcoholic ferric chloride. Acidification of the sodium bicarbonate filtrate gave crude tetrahydroelliptic acid (22 mg.), m. p. 185—190°.

Tetrahydroelliptic Acid.—Methyl tetrahydroelliptate was quantitatively hydrolysed to tetrahydroelliptic acid by warm 0·1N-sodium hydroxide (30 mins.). The acid crystallised on acidification and could be recrystallised from aqueous alcohol, m. p. 202° (Found : C, 60·9; H, 5·6; OMe, 15·9. Calc. for $C_{20}H_{22}O_8$: C, 61·5; H, 5·65; 2OMe, 15·9%), not depressed by tetrahydroelliptic acid prepared from elliptone (preceding paper). The acid gave a deep wine-red colour with alcoholic ferric chloride.

Dehydrotetrahydroelliptone.—Tetrahydroelliptic acid (500 mg.) and sodium acetate (250 mg.) were refluxed in acetic anhydride (10 c.c.) and acetic acid (0·5 c.c.) for 10 mins. Dilution with methyl alcohol (25 c.c.) caused the separation of O-*acetyldehydrotetrahydroelliptone* (203 mg.), which crystallised from chloroform–alcohol in pale yellow plates, m. p. 253° (Found : C, 66·3; H, 5·05; OMe, 15·2. $C_{23}H_{20}O_7$ requires C, 66·6; H, 5·1; 2OMe, 15·6%). The substance was insoluble in alkali and gave no ferric chloride colour. No secondary products could be isolated in a crystalline state.

The acetyl compound (200 mg.) was deacetylated by refluxing with 20% alcoholic hydrochloric acid for 2 hours. Dehydrotetrahydroelliptone (150 mg.) crystallised from alcohol in yellow plates, m. p. 255—260° (decomp.) (Found : C, 67·6; H, 5·3; OMe, 17·4. Calc. for $C_{20}H_{18}O_6$: C, 67·8; H, 5·1; 2OMe, 17·5%), not depressed by dehydrotetrahydroelliptone prepared from elliptone (preceding paper). The dehydro-compound was soluble in aqueous alkali, but gave no colour with alcoholic ferric chloride.

Attempted Synthesis of Elliptic Acid.—The above nitrile (1 g.), 4-hydroxycoumarone (Reichstein and Hirt, *Helv. Chim. Acta*, 1933, **16**, 121) (1 g.) and fused zinc chloride (1 g.) in dry ether (35 c.c.), cooled in ice and salt, were saturated with dry hydrogen chloride. From the hydrolysed product, however, no acid was extracted by sodium bicarbonate.

Methyl Tetrahydromalaccolate.—Methyl 2-cyanomethyl-4 : 5-dimethoxyphenoxyacetate (1·2 g.) and ethylphloroglucinol (2 g.) (prepared by Clemmensen reduction of phloroacetophenone, b. p. 195°/1 mm., m. p. 120°) were condensed together in the presence of zinc chloride (1 g.) as described above for methyl tetrahydroelliptate. The portion of the hydrolysed product insoluble in aqueous sodium bicarbonate was crystallised from aqueous methyl alcohol to give *methyl tetrahydromalaccolate* (690 mg.) in plates, tenaciously retaining solvent, m. p. 184° (Found : C, 59·4; H, 5·75; OMe, 20·6. $C_{21}H_{24}O_9$ requires C, 60·0; H, 5·75; 3OMe, 21·1%). The ester gave a brownish-purple colour with alcoholic ferric chloride. Acidification of the sodium bicarbonate filtrate gave crude tetrahydromalaccolic acid (270 mg.).

Tetrahydromalaccolic Acid.—Methyl tetrahydromalaccolate was hydrolysed to *tetrahydromalaccolic acid* by warm 0·1N-sodium hydroxide (30 mins.). The acid crystallised on acidification, and from 25% aqueous acetone it separated as a dihydrate in plates [Found (after drying over phosphoric oxide in a vacuum desiccator at room temperature) : OMe, 14·0. $C_{20}H_{22}O_9,2H_2O$ requires OMe, 14·0%]. The acid had m. p. 225° and gave a brownish-purple colour with alcoholic ferric chloride (Found : C, 57·0; H, 5·6; OMe, 15·1. $C_{20}H_{22}O_9,H_2O$ requires C, 56·6; H, 5·7; OMe, 14·6. $C_{20}H_{22}O_9$ requires C, 59·1; H, 5·5; OMe, 15·3%).

Dehydrotetrahydromalaccol.—Tetrahydromalaccolic acid (250 mg.) and sodium acetate (125 mg.) were refluxed in acetic anhydride (5 c.c.) and acetic acid (0·25 c.c.) for 10 mins. The reaction mixture was decomposed with water (dilution with methyl alcohol at this stage did not cause the separation of diacetyldehydrotetrahydromalaccol), and the residue treated with warm aqueous sodium bicarbonate. The insoluble portion was crystallised from a small volume of methyl alcohol to give O-*diacetyldehydrotetrahydromalaccol* (30 mg.) in pale yellow needles, m. p. 194—196° (Found: C, 63·0; H, 4·9. $C_{24}H_{22}O_9$ requires C, 63·4; H, 4·9%). The ferric chloride reaction was negative. No other crystalline product could be isolated.

The diacetyl compound (25 mg.) was deacetylated by refluxing with 20% alcoholic hydrochloric acid (3 c.c.) for 2 hours. *Dehydrotetrahydromalaccol* (18 mg.) separated in yellow needles on dilution, m. p. 240° (decomp.) (Found: C, 63·5; H, 4·75. $C_{20}H_{18}O_7,H_2O$ requires C, 63·3; H, 5·0%).

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122. *The Active Principles of Leguminous Fish-poison Plants. Part IX. The Synthesis of Furano*iso*flavones related to Rotenone.*

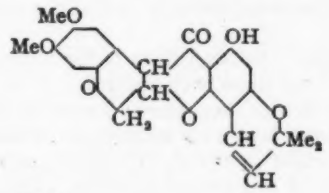
By STANLEY H. HARPER.

By utilising the method of Venkataraman *et al.* (J., 1934, 513, 1120, 1769) *iso*flavones have been prepared from the methyl ethers of derritol, *iso*derritol, and elliptol. In the case of the last, by the isolation of a crystalline intermediate, it is shown that the reaction does not proceed directly to the *iso*flavone but occurs through the formation of an *iso*flavanonol and its subsequent dehydration. *iso*Flavones of this type have been postulated as likely to occur in *Derris* resin along with rotenone and elliptone, with which they are isomeric.

These *iso*flavones are remarkable in giving a positive Durham test, previously regarded as specific for the rotenoids. Their reactions have been studied, and a method devised for the detection of the formic acid formed in their hydrolysis. This method has been applied to the "toxicarol *iso*flavone" isolated from crude toxicarol to establish conclusively its *iso*flavone nature and hence support for the formula previously suggested (J., 1940, 1178).

IN Part V (J., 1940, 1178) a substance was isolated from crude *l*-α-toxicarol (I), isomeric with the latter but containing an additional methoxyl group. As a working hypothesis the *iso*flavone structure (II) was advanced for this substance, which can be referred to as "toxicarol *iso*flavone." If this type of structure could be substantiated, the possibility was realised of there being a series of *iso*flavones isomeric with rotenone, etc., in *Derris* resin.

(I.)



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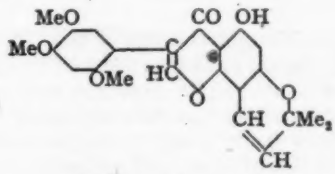

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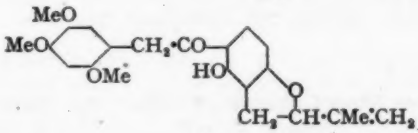

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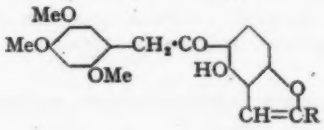
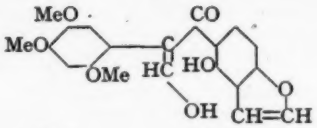
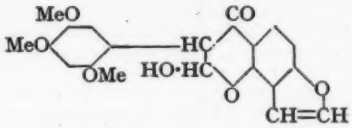


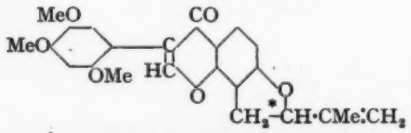
Owing to the comparatively ready availability of the substituted benzyl *o*-hydroxyphenyl ketones, derritol (III), *iso*derritol (IV, R = Pr^{β}), and elliptol (IV, R = H) methyl ethers, it was decided to use the *iso*flavone synthesis by Venkataraman *et al.* (J., 1934, 513, 1120, 1769) in an approach to these problems. Späth and Lederer (*Ber.*, 1930, **63**, 743) postulated an open-chain hydroxymethylene intermediate of type (V), but Venkataraman *et al.* (*loc. cit.*) regarded the condensation with sodium and ethyl formate as proceeding directly to the *iso*flavone. However, recently Wolfrom *et al.* (*J. Amer. Chem. Soc.*, 1941, **63**, 1248) have shown that with osajetin dimethyl ether an intermediate hydroxy-compound is formed, probably an *iso*flavanonol, which loses a molecule of water on subsequent treatment with acetic acid. This formation of a hydroxy-compound has now been observed in the preparation of *iso*flavones from derritol and elliptol methyl ethers. It is therefore probable that in the compounds studied by Venkataraman *et al.* (*loc. cit.*) intermediate *iso*flavanonols were actually formed but dehydrated in the subsequent crystallisation from acetic acid.

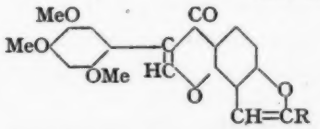
Elliptol methyl ether readily condensed with sodium and ethyl formate at 0°. The product obtained by evaporation of the ethyl formate crystallised in contact with methyl alcohol and so enabled the intermediate to be characterised. This substance contains an additional molecule of water to the *iso*flavone and hence two formulæ appear possible (V and VI). As the substance gives neither a ferric chloride colour nor the Wilson boric acid test (*J. Amer. Chem. Soc.*, 1939, **61**, 2303), the open-chain formula (V) is eliminated and the substance is without doubt represented by the *iso*flavanonol formula (VI). Dehydration of this intermediate was readily effected by refluxing in acetic acid to give *elliptol* iso*flavone* (VIII, R = H). In like manner derritol and *iso*derritol methyl ethers condensed with sodium and ethyl formate to give non-crystalline intermediates which readily dehydrated to the iso*flavones* (VII) and (VIII, R = Pr^{β}) respectively. The former is optically active

owing to the asymmetric carbon atom marked with an asterisk, and this substance is believed to be the first optically active *iso*flavone described.

(V.) 

 (VI.)

(VII.) 

 (VIII.)

As the *iso*flavone from derritol methyl ether contains the *iso*propenyldihydrofuran system characteristic of rotenone, it would be expected to undergo the reactions characteristic of that system. The *iso*flavone readily isomerised to *iso*derritol *iso*flavone (VIII, R = Pr^{β}) in sulphuric–acetic acids with consequent loss of optical activity, a change closely paralleled by the rotenone ⟶ *iso*rotenone change (Wright, *J. Amer. Chem. Soc.*, 1928, **50**, 3355). Hydrogenation of the exocyclic double bond was readily effected in the presence of a palladium–barium sulphate catalyst to give *dihydroderritol* iso*flavone*, but there was no sign of a product analogous to rotenonic acid in which the dihydrofuran ring had suffered fission.

These synthetic *iso*flavones give a positive Durham test when carried out by the spot plate method but not by the procedure of Jones (*Ind. Eng. Chem.*, 1933, **5**, 75), whereas rotenone gives a positive result by both techniques. Nevertheless the fact that these substances with markedly different molecular structures give a positive result considerably lessens the diagnostic value of this test for the rotenoids.

The identity of these substances as *iso*flavones has been fully confirmed by examination of the products of their hydrolysis with aqueous alcoholic alkali. In the case of derritol *iso*flavone, from the acidified hydrolysis solution the open-chain benzyl *o*-hydroxyphenyl ketone, derritol methyl ether, separated in practically quantitative yield, and from the filtrate one mole of formic acid was isolated by steam distillation. In agreement with the observations of Wolfrom *et al.* (*loc. cit.*) these *iso*flavones give the same reduction colour tests described by Asahina *et al.* (*Ber.*, 1928, **61**, 1646; 1929, **62**, 3016; 1931, **64**, 1256) as characteristic of flavones. Hence the detection of formic acid as a hydrolysis product is an essential step in the characterisation of an *iso*flavone.

As a step in the characterisation of the " toxicarol *iso*flavone " isolated from crude toxicarol, the sodium amalgam and magnesium reduction tests for flavones and *iso*flavones have been applied. As with the synthetic *iso*flavones described above, the first test was positive and the second negative. To establish the *iso*flavone nature of this substance it was then necessary to identify formic acid as a hydrolysis product. The above synthetic *iso*flavones being used, a semimicromethod was devised in which the formic acid liberated was separated by steam-distillation and estimated by precipitation of mercurous chloride. This was applied to " toxicarol *iso*flavone " with a clear-cut positive result. Hence the *iso*flavone structure (II) postulated previously is given considerable support.

TABLE I.

(For test insect, carrying medium, and other details, see Table I, this vol., p. 590.) Rel. humidity, 37%.

Substance.	Concn., mg./l.	% Kill.	Substance.	Concn., mg./l.	% Kill.	Substance.	Concn., mg./l.	% Kill.
Derritol *iso*flavone	20	7	Dihydroderritol *iso*flavone	20	5	Rotenone	2	98
	2	9		2	14		1	56
*iso*Derritol *iso*flavone	20	2	Elliptol *iso*flavone	20	24		0·5	33
	2	22		10	27	Control	—	20
				2	20			

With the co-operation of Dr. C. Potter these synthetic *iso*flavones have been compared with rotenone for their possible value as insecticides. The general technique has been described by Potter (*Ann. Appl. Biol.*, 1941, **28**, 142). The kill in the control is unusually large owing probably to the low relative humidity, but the results clearly show that derritol, *iso*derritol, and dihydroderritol *iso*flavones have no significant toxicity even at concentrations ten times that at which rotenone is completely toxic. Elliptol *iso*flavone showed a definite paralytic effect, but the concentration necessary for an adequate kill would render it of no practical interest.

EXPERIMENTAL.

Synthesis of Derritol iso*Flavone* (2′ : 4′ : 5′-*Trimethoxy*-5″-iso*propenyl*-4″ : 5″-*dihydro*-2″ : 3″ : 7 : 8-*furano*iso*flavone*). —Sodium (2·25 g.) was powdered under toluene, and the latter replaced by ether. Dry nitrogen was passed while the flask was cooled in ice and salt. After the ether had evaporated, derritol methyl ether (LaForge and Smith, *J. Amer. Chem. Soc.*, 1930, **52**, 1089) (4·5 g.) was added to the sodium (no reaction), followed by redistilled ethyl formate (45 c.c.) in three portions at 5 minute intervals. The reaction mixture was left in the freezing mixture to warm to room temperature overnight. Water (250 c.c.) was added, and unreacted ethyl formate removed in a current of air. The gum was taken out in ether, washed with water, and evaporated (in a pilot experiment this gummy intermediate could not be crystallised) and the residue refluxed in glacial acetic acid (50 c.c.) for 30 mins. Acetic acid (30 c.c.) was distilled off,

and water added to the residue to give a precipitate of *derritol* iso*flavone*, which crystallised from alcohol (sparingly soluble) in feathery needles, or from benzene in prisms (3·8 g.), m. p. 215°, $[\alpha]_D^{17°}$ −37° in chloroform (c = 1·0) and −60° in benzene (c = 1·0) (Found: C, 70·0; H, 5·6; OMe, 23·4. $C_{23}H_{22}O_6$ requires C, 70·0; H, 5·6; 3OMe, 23·6%). The *iso*flavone was insoluble in 5% aqueous potassium hydroxide and gave no colour with ferric chloride.

Hydrolysis of Derritol iso*Flavone*.—Sodium hydroxide (2·5 g.) was dissolved by warming in water (12·5 c.c.)–absolute alcohol (12·5 c.c.), and derritol *iso*flavone (500 mg.) added. After refluxing for 15 mins., the yellow solution was cooled and acidified with 10% sulphuric acid. Immediate crystallisation occurred and after 2 hours the crop of needles was filtered off, washed free from acid, dried, and recrystallised from methyl alcohol. The derritol methyl ether (451 mg.) so obtained had m. p. 120—122°, not depressed by an authentic specimen (m. p. 122°). Derritol methyl ether gave a deep red colour with alcoholic ferric chloride.

The combined aqueous filtrates (about 250 c.c.) were steam-distilled, the volume being reduced to 25 c.c. and maintained at this level until no further acid distilled over. The free acid in the distillate required 12·75 c.c. of 0·1N-sodium hydroxide (calc. for 1 mol. of formic acid liberated, 12·70 c.c.). The neutralised distillate was evaporated to small bulk, strongly acidified with hydrochloric acid, and reduced with magnesium metal; the solution was then buffered with sodium acetate, and an aqueous solution of dimedon added. Next day the crystalline dimedon derivative of formaldehyde was collected and dried at 60°; m. p. 187°, not depressed by an authentic specimen (m. p. 190°).

Isomerisation to iso*Derritol* iso*Flavone* (2′ : 4′ : 5′-*Trimethoxy*-5″-*iso*propyl-2″ : 3″ : 7 : 8-*furano*iso*flavone*).—Derritol *iso*flavone was not isomerised by sulphuric acid in acetic acid at room temperature. However, it was successfully synthesised under the following conditions: Derritol *iso*flavone (500 mg.) was dissolved in acetic acid (5 c.c.), and sulphuric acid (2·5 c.c.) added without cooling. After 1 hour on the steam-bath, ice was added to the red solution, and the precipitated *iso*flavone collected, dried in a vacuum, and crystallised from methyl alcohol (charcoal). iso*Derritol* iso*flavone* separated in fine needles (337 mg.), m. p. 160°, α_D ±0° in chloroform (Found: C, 69·65; H, 5·7; OMe, 23·4. $C_{23}H_{22}O_6$ requires C, 70·0; H, 5·6; 3OMe, 23·6%).

Hydrolysis of iso*Derritol* iso*Flavone*.—*iso*Derritol *iso*flavone (250 mg.) was hydrolysed with alcoholic sodium hydroxide as described under derritol *iso*flavone. iso*Derritol methyl ether*, obtained by crystallising the precipitate from methyl alcohol, separated in needles (200 mg.), m. p. 125° (Found: C, 68·8; H, 6·4; OMe, 24·2. $C_{22}H_{24}O_6$ requires C, 68·8; H, 6·3; 3OMe, 24·2%). The aqueous filtrate was not examined for the presence of formic acid.

Isomerisation of Derritol Methyl Ether.—Sulphuric acid (0·5 c.c.) was added to derritol methyl ether (105 mg.) in acetic acid (1 c.c.) at room temperature. Next day water was added, and the solid collected and, after drying, crystallised from methyl alcohol (5 c.c.). Needles and nodules separated, but on slight warming the needles dissolved and filtration gave the nodules (27 mg.). This crop had m. p. 200°, was therefore presumably an anhydroderritol and was not further examined. Dilution of the filtrate led to the separation of *iso*derritol methyl ether (38 mg.) in needles, m. p. 125°, not depressed by the specimen prepared above. In an attempt to effect isomerisation on the steam-bath extensive decomposition occurred with the production of water-soluble substances.

Synthesis of iso*Derritol* iso*Flavone*.—*iso*Derritol methyl ether (200 mg.) and sodium (100 mg.) were treated with ethyl formate (2 c.c.) as described under derritol *iso*flavone above. Crystallisation of the product from methyl alcohol gave *iso*derritol *iso*flavone (55 mg.), m. p. 160°, identical with that prepared by the isomerisation of derritol *iso*flavone.

Dihydroderritol iso*Flavone* (2′ : 4′ : 5′-*Trimethoxy*-5″-*iso*propyl-4″ : 5″-*dihydro*-2″ : 3″ : 7 : 8-*furano*iso*flavone*).—Derritol *iso*flavone (1 g.) in ethyl acetate (100 c.c.) was stirred under hydrogen with palladium–barium sulphate catalyst (0·5 g.) (Houben–Weyl, 2nd Edtn., II, p. 270). Absorption of hydrogen corresponding to one double bond was rapid and towards the end of the reduction the product separated. By filtration of the hot solution and crystallisation *dihydroderritol* iso*flavone* (0·83 g.) was obtained; it crystallised from alcohol in needles, m. p. 193°, $[\alpha]_D^{21°}$ −52° in chloroform (c = 1·0) and −67° in benzene (c = 1·0) (Found: C, 69·6; H, 6·25; OMe, 23·4. $C_{23}H_{24}O_6$ requires C, 69·7; H, 6·1; 3OMe, 23·5%). The *iso*flavone was insoluble in 5% aqueous potassium hydroxide.

Synthesis of Elliptol iso*Flavanonol* (2′ : 4′ : 5′-*Trimethoxy*-2″ : 3″ : 7 : 8-*furano*iso*flavanonol*).—Elliptol methyl ether (650 mg.) (this vol., p. 592) and sodium (325 mg.) were treated with ethyl formate (6·5 c.c.) as described under derritol iso*flavone* above. The product obtained by evaporation of the ethyl formate was, however, sparingly soluble in ether and crystallised readily from methyl alcohol in nodules, m. p. 165°. It did not lose water on prolonged drying in a vacuum (Found: C, 65·1; H, 4·9; OMe, 25·0. $C_{20}H_{18}O_7$ requires C, 64·9; H, 4·9; 3OMe, 25·1%). Above the m. p. evolution of gas occurred, probably water vapour.

Synthesis of Elliptol iso*Flavone* (2′ : 4′ : 5′-*Trimethoxy*-2″ : 3″ : 7 : 8-*furano*iso*flavone*).—Elliptol *iso*flavanonol (250 mg.) was refluxed in acetic acid (5 c.c.) for 30 mins.; after dilution with water, the precipitate was collected and crystallised from methyl alcohol, in which it was sparingly soluble, giving *elliptol* iso*flavone* in plates (205 mg.), m. p. 185° (Found: C, 67·7; H, 4·8; OMe, 26·6. $C_{20}H_{16}O_6$ requires C, 68·2; H, 4·6; 3OMe, 26·4%).

TABLE II.

Colour Reactions.

	Rotenone.	Derritol *iso*flavone.	*iso*Derritol *iso*flavone.	Dihydro-derritol *iso*flavone.	Elliptol *iso*flavone.	Elliptol *iso*-flavanonol.	Toxicarol *iso*flavone.
Durham test (procedure that of Harper, J., 1939, 1100)	Blue	Blue-green	Blue-green	Green	Blue-green	Blue-green	Brick-red
Durham test (procedure that of Jones, *Ind. Eng. Chem.*, 1933, **5**, 75)	Blue	—	—	—	—	Blue-green	—
Goodhue test (*J. Assoc. Off. Agric. Chem.*, 1936, **19**, 118)	Red	—	—	—	—	—	—
Sodium amalgam reduction test (cf. *J. Amer. Chem. Soc.*, 1940, **62**, 1488)	—	Red solution, purple ppte.	Red solution	Red solution	Red solution	Red solution	Purple solution, purple ppt.
Magnesium reduction test (cf. *J. Amer. Chem. Soc.*, 1940, **62**, 1488)	—	—	—	—	—	—	—
Sulphuric acid in acetic acid	—	Yellow	Yellow	Yellow	Yellow	Yellow on heating	Yellow

Durham Test.—The following additional substances gave a positive colour reaction with either procedure (*i.e.*, a blue or green colour): Derritol methyl ether, *iso*derritol methyl ether, elliptol methyl ether, derritol, elliptol, derrisic acid, and elliptic acid.

Semimicro-detection of Formic Acid as a Hydrolysis Product of iso*Flavones*.—The synthetic *iso*flavones described above being used, the following method was devised for the detection of formic acid in the alkaline hydrolysis of *iso*flavones and then applied to the "toxicarol *iso*flavone" described earlier (J., 1940, 1178).

10—15 Mg. of the substance were refluxed in 1 c.c. of alkali solution (10% sodium hydroxide in 1 : 1 alcohol–water) for 15 minutes in a flask with a ground joint. A steam distillation head was attached and 25 c.c. of water were distilled over, the contents of the flask being kept at constant volume. After acidification with 10% phosphoric acid (2 c.c.)

the steam-distillation was continued at constant volume until a further 50 c.c. of distillate had been obtained. This distillate was made alkaline with 0·5N-sodium carbonate (0·5 c.c.) and evaporated to dryness in a 50 c.c. flask. The residue was acidified with 10% acetic acid (0·5 c.c.), 10 c.c. of saturated mercuric chloride in 2% acetic acid added, and the flask stoppered and heated in a boiling water-bath for 2 hours. The precipitated mercurous chloride was collected in a small Gooch crucible, washed with N-hydrochloric acid, water, and 95% alcohol, and dried at 100° for 30 mins.

Formic acid (1 mg.) quantitatively precipitated mercurous chloride (10·2 mg.) with this reagent (cf. Miles and Pirie, *Biochem. J.*, 1939, **33**, 1709).

Derritol *iso*flavone (11·9 mg.) gave 6·55 mg. of mercurous chloride (Found: formic acid, 5·4. Calc. for $C_{23}H_{22}O_6$, 11·7%. Recovery, 46%).

Toxicarol *iso*flavone (13·7 mg.) gave 8·20 mg. of mercurous chloride (Found: formic acid, 5·8. Calc. for $C_{23}H_{22}O_7$, 11·2%. Recovery, 56%).

Rotenone and *dl*-α-toxicarol gave no formic acid under the above conditions. The recovery of formic acid by steam-distillation of a limited volume is incomplete, but in the two cases the percentage recovery is of an order consistent with the formulæ given to them.

I am indebted to Dr. C. Potter for carrying out the biological trials recorded in this and the previous paper and to the Ministry of Agriculture and the Colonial Development Fund for grants.

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123. *The Kinetics of the Reaction between Copper and Iodine in Aqueous (Potassium Iodide) Solution. Part I.*

By L. LEIGHTON BIRCUMSHAW and MAURICE H. EVERDELL.

The reaction between copper and iodine solutions containing initially iodine and potassium iodide in the ratio 1 atom. : 4 mols. has been studied and the following points have been established: (1) For a large range of concentrations of iodine the rate of reaction is unaffected by the presence or thickness of the cuprous iodide film formed on the copper as a result of the reaction; (2) the reaction is unimolecular with respect to the iodine; (3) when the reaction proceeds at constant concentration of iodine the graph of time against weight of cuprous iodide is a straight line; (4) the reaction rate is unaffected by the method of preparation or degree of smoothness of the metal surface or by the presence of a cuprous oxide film formed on the copper at 100°; (5) from the temperature coefficient the "critical increment" has been calculated to be 6500 cals. per g.-atom; (6) in the case of N/50-solutions of iodine, if over 300 g./l. of potassium iodide are present the cuprous iodide is not deposited as a film on the metal but is retained in solution, the copper being left in a finely etched condition and oxidising rapidly on drying in the air; (7) the increase in reaction rate on increasing the potassium iodide concentration over a large range of concentrations has been identified with the increase in the rate of diffusion of iodine in higher concentrations of potassium iodide; (8) it is believed that the reaction proceeds by the passage of both iodine and solvent through the cuprous iodide film, and not by the diffusion of copper.

EARLY work on the reaction between aqueous potassium iodide and certain metals including copper was carried out by Van Name and his collaborators (Van Name and Edgar, *Amer. J. Sci.*, 1910, **19**, 45, 237; 1911, **32**, 207; 1917, **43**, 449), who considered that the rates of solution of mercury, cadmium, zinc, copper, and silver in aqueous solutions of iodine containing a large excess of potassium iodide are practically equal, as would be anticipated according to Nernst's diffusion theory. The temperature coefficient between 10° and 35° was found to be 1·3. Increase of potassium iodide concentration accelerated the reactions. In the case of copper and silver large quantities of potassium iodide were used to dissolve the cuprous and silver iodides, as Van Name wished to study the reaction without the presence of the iodide film which he considered would lower the rate of solution of the metal.

For all the metals investigated his method was the same. Strips of the metal foil were placed in the liquid which was stirred at a fixed rate, and the course of the reaction was followed by titration of portions of the solution withdrawn at definite time intervals. The method involved a change of volume of the solution from step to step. If v = volume of solution at a time t, m = total weight of available iodine, c = concentration of iodine, and the reaction is unimolecular with respect to the iodine, the rate of reaction will be defined by $k = [v/(t_2 - t_1)] \log_e c_1/c_2$. This equation was found to hold, and values of k were found to be approximately equal at 25° for all the metals investigated; Van Name therefore considered that the rates of reaction were governed by the rate of diffusion of iodine in the solution.

More recently, interest has centred in the function of the films formed on metal surfaces as the result of chemical action. Pilling and Bedworth (*J. Inst. Met.*, 1923, **29**, 529) have postulated that in many cases in the oxidation of metals the rate of reaction is controlled by the diffusion of oxygen through the protective layer of oxide film formed on the metal surfaces. Hence at constant concentration of oxygen, if x is the mass of the gas combined with the metal at the time t, the rate of reaction $dx/dt = k/x$ which integrates to $\frac{1}{2}x^2 = kt$. This well-known parabolic law, sometimes called the Tammann–Pilling–Bedworth equation, has been found to hold for many cases of corrosion, oxidation, and reactions giving a film of reaction product on the surface of the solid reactant.

Evans and Bannister (*Proc. Roy. Soc.*, 1929, *A*, **125**, 370) have recorded results of experiments on the reaction between silver and iodine in various organic solvents. With constant concentration of iodine, the parabolic law is obeyed save for very small thicknesses of silver iodide. From the effect of concentration it was concluded that the state of the iodine adsorbed on a layer of the silver is not less than I_2 but the small temperature coefficient excludes the idea of "gaseous" diffusion through large apertures. The effect of varying the

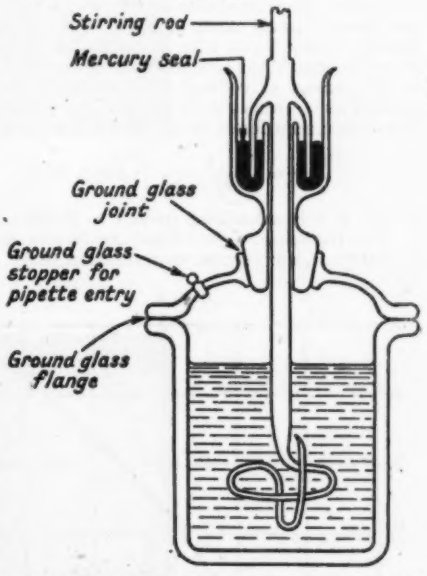
solvent indicated that the process is not controlled by the solvent entering pores, and they considered that the iodine passes through pores of a few molecular diameters in loose union with the silver iodide, a process intermediate in character between diffusion in solid solution and gaseous leakage through definite cracks.

The reaction between copper and sulphur in carbon tetrachloride solution has been studied by Bradley (*Trans. Faraday Soc.*, 1938, **34**, 278), who found that, although a film of cuprous sulphide was deposited on the copper surface, the reaction was unimolecular with respect to the sulphur concentration and the film did not affect the rate.

In general, it appears that heterogeneous reactions which result in formation of a film on the surface of one reactant fall into two classes: (i) in which the velocities are controlled by the diffusion of one or more reactants through the film; (ii) in which the rate is independent of the thickness of the reactant film. Interest in this question has recently been revived by the work of Wagner (*Z. physikal. Chem.*, 1933, *B*, **21**, 37) on the reaction between silver and sulphur at 400°; he concluded that, contrary to expectation, it is mainly the silver, and not the sulphur, which diffuses through the film of silver sulphide. A similar phenomenon was noted previously by Pfeil (*J. Iron Steel Inst.*, 1929, **119**, 501), who showed that in the oxidation of iron there is considerable diffusion outwards through the already existing film of oxide.

The present work records values of the rates of reaction between copper and iodine dissolved in aqueous potassium iodide, and the following variables were investigated: (1) The initial concentration of the iodine, from 0·04N to 0·0025N; in all cases unless otherwise stated the solutions contained 4 mols. of potassium iodide per atom of iodine. (2) The nature and treatment of the surface of the copper foil. (3) The concentration of the potassium iodide. (4) The temperature, 20°, 25°, 30°, and 35°. (5) The rate of stirring. One of the chief objects was to obtain information on the influence of the cuprous oxide film on the course of the reaction, especially with regard to Wagner's work.

FIG. 1.



EXPERIMENTAL.

Materials.—"AnalaR" Iodine (Hopkin and Williams) was used throughout. The impurities consisted only of 0·01% non-volatile matter, 0·005% chloride and bromide, 0·005% cyanide, 0·01% sulphate, so further sublimation over potassium iodide was considered unnecessary. "AnalaR" Potassium iodide was also used, and the "AnalaR" sodium thiosulphate contained sulphate and sulphite 0·01%, sulphide 0·0005%, heavy metals 0·0015%. The copper foil was of extremely high purity and was kindly supplied by I.C.I. Metals, Ltd., through the courtesy of Dr. Maurice Cook. All burettes and pipettes were checked by gravimetric means, and one pipette was used throughout the entire work for the withdrawal of the 5-c.c. samples.

Preparation of the Copper Surface.—Pieces of copper 4·0 × 4·5 cm. and 0·25 mm. thick, were used. This thickness ensured a strong foil which would not bend on rapid rotation in the liquid, yet the total weight of metal was small enough to ride easily in the fragile glass saddle. The standard polished surface was always prepared as follows except where otherwise stated. The copper was cut into the requisite area by means of a razor blade and a copper guide block of accurate dimensions. The foil was then washed free from grease with carbon tetrachloride. A pad of washed linen containing carborundum powder grade 3F was soaked in carbon tetrachloride and used to polish the metal in one direction only for 3 mins. on each side of the foil. This method ensured the removal of all surface impurities and oxide. The foil was then well washed with carbon tetrachloride and kept under the liquid until used. In every case the foil was prepared immediately before the start of each experiment. This method of polishing will be referred to as "carborundum straight polishing" (C.S.P.).

Apparatus.—The reaction vessel is shown in Fig. 1 and is self-explanatory. The metal specimen is held in the saddle, constructed from drawn-out glass rod (0·1 cm. thick), so that the edges of the specimen only touch the glass at three points. The vessel is made completely of glass, with ground glass flanges and joints, and the interior is closed by a mercury seal. The area of mercury exposed to iodine vapour within the vessel is so small as to be negligible. The vessel is readily opened by sliding the part above the ground glass flange, and the glass stopper in the top portion exists for the entry of the pipette. This stopper is removed momentarily at given intervals, but the duration of each removal is so small that no appreciable evaporation takes place.

The rotation of the stirrer was effected by an electric motor connected to the glass rod through a reduction gear. This ensured more regular rotation than if no reduction gear were used, and by introducing a rheostat into the motor circuit the rate of rotation could be varied to obtain close reproduction of results.

In all experiments, except those carried out in constant concentration of iodine, the procedure was the same. 300 C.c. of the solution were measured into the reaction vessel, which was immediately closed and placed in the thermostat at the particular temperature. At the start of the reaction the copper foil was placed in the saddle, and rotation carried out at a fixed rate. At given intervals 5 c.c. samples were pipetted out and titrated directly with sodium thiosulphate solution, the concentration of which was ½ that of the initial concentration of the iodine solution. The initial titration figure (20 c.c.; $t = 0$) was large enough to ensure a reasonable accuracy. The titrations of iodine by thiosulphate entailed using solutions of the latter between ranges of concentration of N/100 and N/1600. It was found that the use of such dilute solutions in no way vitiated the accuracy of the titrations. Very dilute starch solutions were used and the pale sky-blue colour disappeared with extreme sharpness at the end-point.

Analysis of the Film.—A piece of copper foil was cleaned and polished (C.S.P.) and rotated in an N/100-solution of iodine in N/25-potassium iodide for 1 hour. It was then removed, washed, and dried, and the film removed and its copper content determined by the thiocyanate method (Found: Cu, 33·28. Calc. for Cu_2I_2: Cu, 33·34%).

The Direction of Diffusion through the Film of Cuprous Iodide.—Wagner's method (*loc. cit.*) failed, for whereas silver

sulphide forms stable, hard pellets, those formed when cuprous iodide is compressed are soft and crumble readily. An alternative method was therefore tried. When copper reacts with iodine, the resulting film has a faint yellow tinge if aqueous potassium iodide is the solvent, but is almost colourless if thiophen-free benzene is the solvent. If, however, iodine solution in benzene containing slight traces of thiophen is used, the resultant film is black. This may be due to the presence of minute traces of cuprous sulphide in the film, but the amount is too small to be detected.

Two sheets of copper foil were polished (C.S.P.). A double saddle was constructed on the end of the stirring rod, and one piece of copper placed in each compartment. These were rotated in an N/100-solution of iodine in benzene (not thiophen-free) for 24 hours, and a stable black film was formed over the surface of both pieces of copper. These were removed and dried. One specimen was then rotated in N/200-iodine in N/50-potassium iodide for 20 minutes, removed, and dried. Inspection of the primary film showed it to be black throughout. The film on the further-treated specimen, however, showed a black outer film characteristic of the action of iodine in benzene, and underneath, an inner white film characteristic of the action of aqueous iodine. A portion of the outer black film was chipped off with a razor and a photomicrograph is shown in Fig. 2. The black film is superimposed on the white film. In the bottom left-hand corner a little of the white film has also been broken away and shows the copper surface underneath. Apparently the iodine diffuses through the film to the copper.

The experiment was then reversed. Two copper sheets were prepared as before and rotated in a similar iodine solution, two stable white films being produced. The foils were removed and dried, and one was rotated in a solution of iodine in benzene for 36 hours, removed, and dried. The first specimen showed a homogeneous white film, but the second showed, beneath this white film, a black film characteristic of the action of iodine in benzene. A photomicrograph of the foil, with a portion of the white film chipped away, is shown in Fig. 3. Here again the iodine appears to diffuse through the cuprous oxide film. It must be remembered that the reaction for which Wagner showed a reverse mechanism, *i.e.*, the diffusion of the cation rather than the anion, takes place at a high temperature (400°).

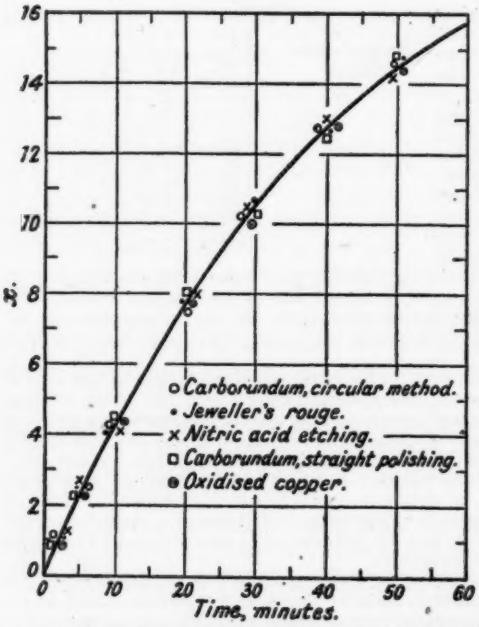
Table I shows the complete readings for the reaction with solutions of iodine of initial concentration N/400 at 25°. For other concentrations at 25° and a number of experiments at 20°, 30°, and 35°, only the times and the values of k are given. In all cases, [KI]/[I] = 4. Col. 2 gives the thiosulphate titration ($a - x$). Col. 3 gives c, iodine concentration (g.-atoms/l.) at time t, calculated from the titration value. Col. 4 shows x, which is proportional to the amount of iodine which has reacted with the copper at time t save for a small correction to be made in each reading for the effect of the change of volume after each titration. In col. 5, χ represents the total amount of iodine (in g.-atoms $\times 10^{-6}$) present as cuprous iodide per sq. cm. of copper surface at time t, corrections having been made for the change in volume of solution mentioned above and for the area of copper (36 sq. cm.), as given by

$$\chi = \frac{1}{1000 \times 36}\left\{\left(300c_0 \times \frac{x_1}{20}\right) + \left(295c_0 \times \frac{x_2 - x_1}{20}\right) + \left(290c_0 \times \frac{x_3 - x_2}{20}\right) \quad . \quad . \quad . \quad . \quad . \right\}$$

In Col. 6, k is calculated from $k = [2{\cdot}303v/(t_2 - t_1)] \log_{10} c_1/c_2$.

The Influence of the Copper Surface on the Rate of the Reaction.—The method of polishing the copper surface has been described. Microscopic examination (mag. 50) showed unbroken parallel scratches on the metal. Three other methods for the preparation of the surface were used, and their effect on the reaction rate investigated. (1) The surface was washed as before and a similar pad made. The polishing was carried out, however, with a circular motion. The strip was then washed again as in the first method. Surfaces so treated showed under the microscope deep scratches. (2) The copper surface was washed with carbon tetrachloride and first polished with a revolving pad of washed lamb's wool and soft brick dust. Final polishing was carried out with jeweller's rouge. The final surface showed excellent optical reflection and no scratches (mag. 50). (3) The surface was washed with cotton wool soaked in very dilute nitric acid until it was of uniform colour, then washed well with water and finally with carbon tetrachloride. Surfaces so prepared showed no scratches.

FIG. 4.



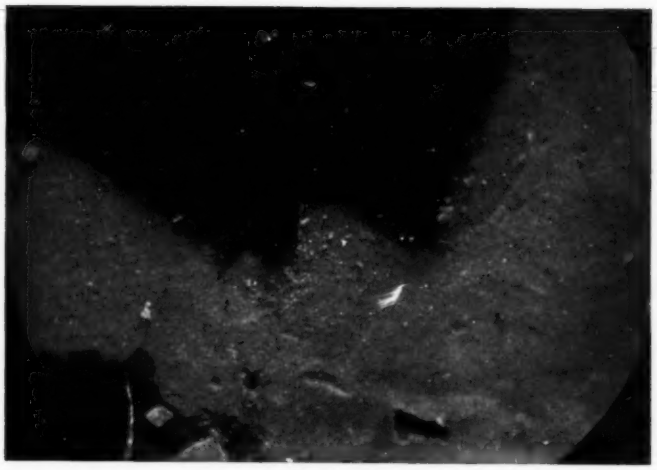
Vernon (J., 1926, 2273) has shown that when copper is heated in air for a short time at 100° a film of oxide is formed, which has extraordinary protective properties. It was considered of interest to determine if this film had any influence on the present reaction. A deep red film was produced on the metal by heating it for 30 mins. in a closed glass vessel in an air-bath at 100°. Care was taken not to damage the film in removal.

All these differently prepared specimens were tested in $N/50$-iodine at 25°. The results are shown graphically in Fig. 4, x being plotted against t; x is comparable in all cases, and it will be seen that the preparation of the copper surface has no effect on the rate of reaction. If, after a few minutes' reaction between the oxidised copper and the iodine, the cuprous iodide layer be removed with a razor, no sign of the oxide film can be seen. Probably this very thin oxide film is immediately removed by iodine.

The Reaction in Solutions containing Large Quantities of Potassium Iodide.—It has been shown by Van Name and Edgar (*loc. cit.*) that if copper reacts with iodine containing about 400 g. of potassium iodide per l., cuprous iodide is not deposited but remains in solution. Such a solution of potassium iodide was therefore used in studying the reaction at four temperatures, 20°, 25°, 30°, and 35°, the object being to compare the rate of reaction with the rates in solution of low iodide concentration where the iodide film is present. The surface of the metal after reaction presented some features of interest: it was completely free from cuprous iodide but pale pink and very rough. On washing and drying the metal and examining it in air, the surface was found to be reddish-brown, probably owing to oxidation, the surface of the copper being so pitted that when the layer of protective moisture evaporated, the copper surface spontaneously oxidised. The results are shown in Table II. The column headed χ has a slightly different significance and may be considered to represent the weight of iodine lost from solution as I_2 or KI_n per sq. cm. of copper surface.

The Reaction at Constant Concentration of Iodine.—The experimental difficulties of keeping the concentration of iodine in solution constant throughout are considerable. Since these experiments preclude following the reaction by titration, it must be followed by weight increments. The use of a large concentration of iodine and small strips of copper would

FIG. 2.



Magnification 50 diameters.

FIG. 3.

Magnification 50 diameters.

[*To face p.* 600.

TABLE I.

N/400-*Iodine at* 25°.

Time, mins.	$(a-x)$.	$c \times 10^5$.	x.	$\chi \times 10^6$.	k.	Time, mins.	$(a-x)$.	$c \times 10^5$.	x.	$\chi \times 10^6$.	k.
0	20·0	250	—	—	—	20	12·4	155	7·6	7·619	7·74
2	19·1	239	0·9	0·937	6·91	30	9·6	120	10·4	10·292	7·05
5	17·9	224	2·1	2·166	6·38	40	7·3	91	12·7	12·449	7·39
10	15·8	197	4·2	4·282	7·23	50	5·7	71	14·3	13·921	6·56
15	14·0	175	6·0	6·063	6·80	60	4·4	55	15·6	15·094	6·72
										Mean	6·99

N/200-*Iodine at* 25°.

Time, mins.	k.
2	6·99
5	6·93
10	6·91
15	6·89
20	7·23
30	7·09
40	7·12
50	6·95
60	6·86
Mean	6·99

N/100-*Iodine at* 25°.

Time, mins.	k.
2	6·91
5	6·66
10	6·91
15	7·07
20	6·79
30	7·03
40	7·03
50	7·37
60	6·86
Mean	6·96

N/50-*Iodine at* 25°.

Time mins.	k.
2	6·91
5	6·59
10	6·93
15	7·32
20	6·59
30	7·30
40	7·00
50	7·25
60	6·54
Mean	6·97

N/25-*Iodine at* 25°.

Time, mins.	k.
2	6·15
5	6·38
10	6·84
15	7·21
20	6·75
25	7·02
30	6·84
40	7·16
50	7·24
60	6·75
Mean	6·83

N/400-*Iodine at* 20°.

Time, mins.	k.
2	6·22
5	5·11
10	5·41
15	6·07
20	5·76
30	5·62
40	5·92
Mean	5·73

N/200-*Iodine at* 20°.

Time, mins.	k.
2	5·78
5	4·84
10	5·18
15	6·22
20	5·53
30	5·80
40	5·57
Mean	5·56

N/100-*Iodine at* 20°.

Time, mins.	k.
2	5·71
5	5·39
10	5·94
15	5·39
20	5·85
30	6·08
40	6·15
Mean	5·78

N/50-*Iodine at* 20°.

Time, mins.	k.
2	5·35
5	5·51
10	5·49
15	6·09
20	5·50
30	5·85
40	6·21
Mean	5·71

N/25-*Iodine at* 20°.

Time, mins.	k.
2	5·71
5	5·51
10	5·67
15	5·61
20	5·69
30	5·61
40	5·84
Mean	5·66

N/400-*Iodine at* 30°.

Time, mins.	k.
2	7·12
5	8·89
10	7·69
15	7·83
20	9·45
30	8·87
40	—
Mean	8·31

N/200-*Iodine at* 30°.

Time, mins.	k.
2	7·70
5	8·24
10	8·77
15	8·35
20	8·55
30	8·79
40	8·35
Mean	8·38

N/100-*Iodine at* 30°.

Time, mins.	k.
2	8·08
5	8·41
10	8·22
15	8·32
20	8·31
30	8·36
40	8·09
Mean	8·21

N/50-*Iodine at* 30°.

Time, mins.	k.
2	8·49
5	8·13
10	8·61
15	8·16
20	8·10
30	8·20
40	8·48
Mean	8·31

N/400-*Iodine at* 35°.

2	9·30
5	9·80
10	9·63
15	9·92
20	10·12
30	10·08
Mean	9·81

N/200-*Iodine at* 35°.

2	9·68
5	10·22
10	9·69
15	9·99
20	9·65
30	9·69
Mean	9·82

N/100-*Iodine at* 35°.

2	8·75
5	9·99
10	10·57
15	9·17
20	10·59
30	9·89
Mean	9·827

N/50-*Iodine at* 35°.

2	8·75
5	9·59
10	9·16
15	10·71
20	10·96
30	9·98
Mean	9·86

not give results of sufficient accuracy, since the weight increments would be so small. It is impossible to use a saturated solution of iodine in, say, N/200-potassium iodide solution, with solid iodine present in a linen bag, since its rate of dissolution in this solution is smaller than its rate of consumption by the reaction.

The following method was found satisfactory. About 25 c.c. of chloroform were placed in the bottom of a standard reaction vessel, and excess iodine added, giving a saturated solution. 300 C.c. of N/200-potassium iodide were added, and equilibrium was established by stirring with a glass sheet in the rotation saddle used previously for the copper strip. A certain concentration of iodine was set up, according to the partition coefficient, in the aqueous layer. The requisite number of copper strips were prepared (36 sq. cm. area), polished (C.S.P.), washed, dried, and weighed. When the solution had reached equilibrium the glass sheet was replaced by a copper strip, and the reaction carried on for a time t, the copper then being removed, washed, dried, and weighed. A second copper strip was then rotated for a time t_2, and so on. That the concentration of the iodine in the aqueous layer remained constant throughout was checked by titrations with thiosulphate. The equilibrium between saturated chloroform and N/200-potassium iodide was restored more rapidly than the iodine was removed by the reaction. These experiments were repeated with N/400-potassium iodide, and the temperature in each case was 35°. The results are shown graphically in Fig. 5, and it will be seen that the relation between weight increment and time is linear.

TABLE II.

(c_0 = 0·0200 throughout.)

Time, mins.	$(a-x)$.	$c \times 10^4$.	x.	$\chi \times 10^6$.	k.	Time, mins.	$(a-x)$.	$c \times 10^4$.	x.	$\chi \times 10^6$.	k.
		N/50-*Iodine at* 20°.						N/50-*Iodine at* 25°.			
2	19·2	192	0·8	6·67	6·12	2	19·05	190	0·95	7·92	7·31
5	17·9	179	2·1	17·32	6·89	5	17·6	176	2·4	19·80	7·78
10	15·9	159	4·1	33·43	6·87	10	15·35	153	4·65	37·92	8·11
15	13·95	139	6·05	48·87	7·45	15	13·35	133	6·55	53·76	7·79
20	12·25	122	7·75	62·09	7·29	20	11·5	115	8·5	68·15	8·35
30	9·55	95	10·45	82·72	6·84	30	8·4	84	11·6	91·83	8·65
				Mean	6·91					Mean	8·01
		N/50-*Iodine at* 30°.						N/50-*Iodine at* 35°.			
2	18·8	188	1·2	10·00	9·19	2	18·6	186	1·4	11·67	10·89
5	17·15	1715	2·85	23·52	9·23	5	16·75	167	3·25	26·85	10·30
10	14·55	1455	5·45	44·46	9·44	10	13·65	136	6·35	51·80	11·87
15	12·3	123	7·7	62·27	9·79	15	11·3	113	8·7	70·40	10·77
20	10·3	103	9·7	77·82	9·86	20	9·25	92	10·75	86·34	11·21
30	7·3	73	12·7	100·75	9·51	30	6·1	61	13·9	110·40	10·44
				Mean	9·50					Mean	11·08

Retarding Films.—Evidence has been given that the film of cuprous iodide formed by the action of aqueous iodine on copper does not retard the reaction. In certain cases, however, retarding films have been observed and they may be divided into two sections.

FIG. 5.

Reaction between copper and iodine of constant concentration at 35°.

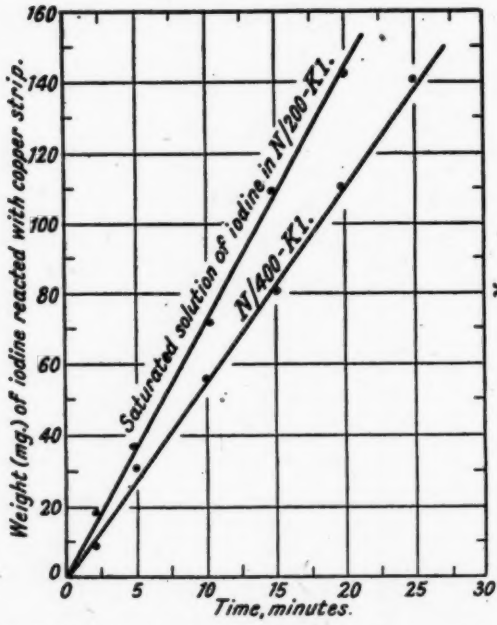
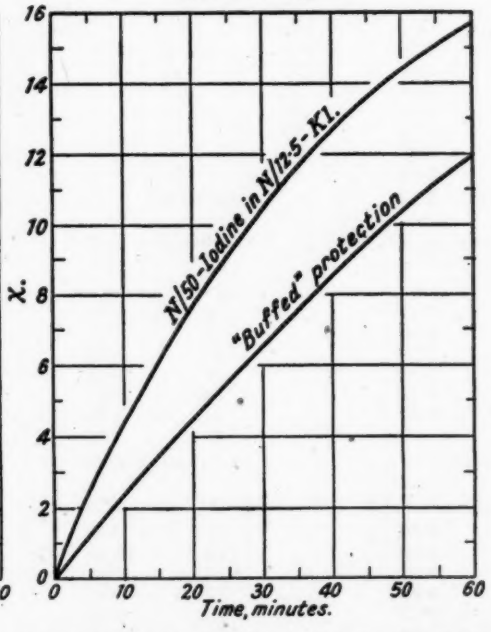


FIG. 6.

Graph showing retardation of reaction by buffing cuprous oxide film.



(1) *"Buffed" surfaces.* A piece of copper was prepared in the usual manner, placed in N/25-iodine in N/6·25-potassium iodide solution for 1 hour, removed, and dried. The surface was then "buffed" with the usual carborundum pad. Much of the outer film was removed, but the copper strip showed a brown lacquer-like finish. The strip was then tested with N/50-iodine solution as usual. The results are shown graphically in Fig. 6. It will be seen that with the "buffed" metal the reaction is slower. In some way a part of the iodide is ground into the copper surface and forms a partly protective layer. The protective nature of such a treatment was found in all cases investigated, and in one experiment the buffing produced a protective layer which almost prevented further action on the metal by aqueous iodine solution.

(2) *Rapidly deposited films.* In the foregoing tables, the readings for the reaction between copper and N/25-iodine in N/6·25-potassium iodide at 30° and 35° are omitted. They are given in Tables III and IV. In Table III k is fairly

TABLE III (30°).

Time, mins.	$a-x$.	k.	Time, mins.	$a-x$.	k.
0	20·0	—	15	14·2	6·54
2	19·2	5·80	20	12·75	5·89
5	17·9	6·98	30	10·55	5·29
10	15·9	6·96	40	8·9	4·59

TABLE IV (35°).

Time, mins.	$a-x$.	k.	Time, mins.	$a-x$.	k.
0	20·0	—	15	13·3	6·17
2	18·75	9·68	20	12·1	5·39
5	17·0	9·63	30	10·25	4·51
10	14·8	8·04	40	8·75	4·35

constant but lies well below the figure for 30° (8·31) obtained with the lower concentrations. In Table IV, k starts slightly below the value for 35° (lower concentrations), *viz.*, 9·83, and falls rapidly with time. This phenomenon was duplicated on repeating these experiments. That is, the reaction with N/25-iodine does not obey the simple unimolecular law followed over the more dilute range of concentrations at these and lower temperatures. These solutions are the most concentrated used previously, so that the experiments at 30° and 35° are those in which the cuprous iodide film is most rapidly formed in its initial stages. In view of this, the reaction was studied with N/10-iodine in N/2·5-potassium iodide solution at 35°, 30°, 25°, and 20°. In all cases the velocity constant falls off rapidly with time, and the rate of fall increases with rise of temperature; moreover, all the cuprous iodide films are harder and less easily chipped away than the usual films. Table V shows M, the amount of iodine (g.) absorbed in 30 mins. from different concentrations at 25° and 30°.

TABLE V.

At 25°.

Initial concn. of iodine, N	0·0025	0·005	0·01	0·02	0·04	0·1
M, g.	0·0475	0·0950	0·1882	0·3800	0·7434	0·8055

At 35°.

Initial concn. of iodine, N	0·0025	0·005	0·01	0·02	0·04	0·1
M, g.	0·0589	0·1170	0·2367	0·4750	0·7115	0·8360

The Concentration of the Potassium Iodide.—The reaction between N/50-iodine in potassium iodide solution of concentrations (g./l.) 13·28 (N/12·5), 50, 100, 150, 200, 300, 400, and 800 was carried out in the usual manner at 25°. The

FIG. 7.

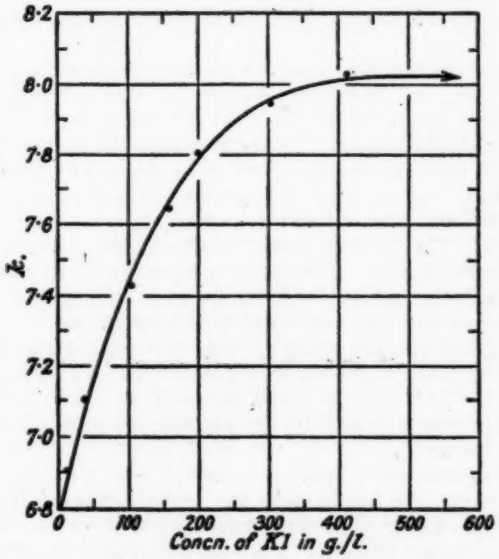
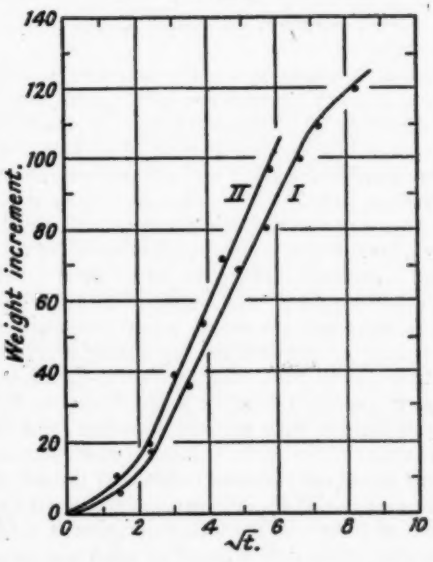


FIG. 8.



results are shown graphically in Fig. 7. With 200 g. of potassium iodide the film becomes patchy and shows evidence of having been partly attacked by the iodide. With 300 g. of potassium iodide no film of cuprous iodide is visible. Examination of the graph shows that the velocity constant increases gradually with increase of potassium iodide concentration up to 400 g./l., no further difference being shown at 800 g./l.

Rate of Stirring.—The effect of the rate of stirring on the rate of reaction was investigated but no change was detected as long as the rotation was maintained at a fairly high rate. A standard rate of 100 r.p.m. was adopted as giving reproducible results.

DISCUSSION.

The reaction which has been studied might be governed by any of the following mechanisms. (1) The rate might be independent of the concentration of iodine throughout, and controlled by diffusion of iodine through the film of cuprous iodide, in which case the reaction will follow the Tammann–Pilling–Bedworth equation $dx/dt = k/x$, whence $x^2 = kt$. (2) The rate might be independent of the thickness of the cuprous iodide layer but directly proportional to the concentration of the iodine. Hence, dealing, as we are here, with a constant surface area of copper, a unimolecular law, modified for the step-wise volume changes introduced in the course of the reaction, might apply; *i.e.*, $k = [v/(t_2 - t_1)] \log_e c_1/c_2$. (3) The rate might be proportional to the concentration of the iodine at any moment and might also be controlled by diffusion through the cuprous iodide layer so that $-dc/dt = kc/\chi$, where χ is proportional to the thickness of the iodide layer.

In Fig. 8 graphs for 25° of the weight increment against $t^{\frac{1}{2}}$ are shown. Curve I represents N/50-iodine in N/12·5-potassium iodide; Curve II shows the reaction with N/50-iodine in aqueous potassium iodide containing 400 g./l. Curve I after a short initial period approximates to a straight line, and it might be assumed from this that the Tammann–Pilling–Bedworth law is approximately obeyed. When Curve II, *representing the reaction*

in the absence of an iodide film, is considered, however, the graph is seen to be of the same shape. Again, if the course of the reaction in dilute potassium iodide be governed by mechanism (1), the rate of reaction being independent of the concentration of iodine in solution, then the values of χ at any time t, in cases involving different initial concentrations of iodine solution, should be identical. This is not so: the values of χ are directly proportional to the initial concentration of iodine. The simple Tammann–Pilling–Bedworth equation is not therefore applicable to this reaction under our conditions.

The results given in Table II show that the equation $k_2[v/(t_2 - t_1)] \log_e c_1/c_2$, first derived by Van Name and Edgar, is obeyed quite well. The values of k increase slowly with rise of temperature, as observed by Van Name and Edgar. Consideration of the results of experiments in Table I shows, however, that the equation is equally well obeyed in those cases in which the copper is covered with a cuprous iodide film throughout the reaction. The value of k will be seen to be approximately independent of the initial concentration of the iodine, and it is concluded that, between the limits of temperature and under the conditions stated, the reaction between copper and iodine dissolved in aqueous potassium iodide is unimolecular with respect to the iodine and is independent of the presence or thickness of the cuprous iodide film formed on the copper in the course of the reaction.

It may be suggested therefore that the reaction proceeds by collisions between the iodine and the copper surface. The film of iodide has no impeding effect; hence the reactant appears to pass through the film readily. This is not unexpected, since cuprous iodide films so formed are easily wetted by water.

The physical condition of the surface of the copper does not affect the reaction rate. If the reaction were controlled by the diffusion of one reactant through the film, then it might be expected that the type of surface would affect the reaction rate; for various types of surface might initiate a particular orientation of the film of iodide. Since, however, the reaction is not controlled by diffusion through the film the results obtained are not unexpected.

The gradual increase in k with increase in iodide concentration in the reaction between various metals and iodine in aqueous potassium iodide was noted by Van Name and Edgar (*loc. cit.*). The problem was investigated further by Edgar and Diggs (*J. Amer. Chem. Soc.*, 1916, **38**, 253), who measured the rate of diffusion of iodine in potassium iodide solutions of various concentrations at 25°. They give a graph showing the relation between the diffusion constant and the concentration of the iodide which is similar in shape throughout its whole course to that of Fig. 7. The conclusion they reached, confirmed by the present work, is that the increased rate of reaction is connected in some way with the increased rate of diffusion of the iodine.

We now consider the more rapidly deposited films. The readings at 25° (Table V) show that the value of M for a 0·005N-solution is twice the value for the 0·0025N-solution. This direct proportionality holds up to and including 0·04N-solution. The value of M for 0·1N-solution is, however, barely greater than that for 0·04N-solutions, and moreover the reaction in 0·1N-solution does not obey the simple unimolecular law. The readings at 35° show strict proportionality up to and including 0·02N. The value of M for 0·04N-solutions is, however, much less than twice the value for 0·02N-solutions, and the value for 0·1N-solution is still further removed from the value expected if strict proportionality held. The reaction at 25° in solutions up to and including 0·04N is unimolecular with respect to iodine, but this does not hold at higher concentrations. At 35° this mechanism breaks down when solutions of 0·04N are reached.

For many reactions between solids and liquids it is considered that an adsorbed film of reactant is set up on the surface of the solid—Nernst's well-known theory. We might make the probable assumption that the concentration of iodine in the adsorbed layer is a function of that in the solution up to a certain value of the latter, after which it is independent of the bulk concentration of iodine. We should expect the reaction to be unimolecular up to this point, after which the velocity of the reaction would become constant (zero order). These assumptions would not explain such a result as that obtained at 35° with N/25-iodine (Table IV), where the unimolecular constant starts off at approximately the " correct " figure and falls rapidly with time. Although under the conditions of temperature and concentration detailed in Table I, the rate of reaction is not affected by the presence of the iodide film, yet it is possible that under conditions in which the film forms on the copper at a much greater rate, the structure of the film may be altered. It may be that, during relatively slow growth of the cuprous iodide, intercrystalline cracks and holes may exist in the film and these permit the passage of the reactant readily. During rapid film growth, however, these holes may be covered by further crystals laid haphazardly upon them. We have also the possibility of orientation of the crystals composing the film occurring at some rate of formation of the latter. *X*-Ray examination should throw some light on this question. We have, however, the experimental observations that the films produced at the higher concentration (Table IV) appeared harder and less easily removed from the metal than the usual films.

It is well known that apparently simple heterogeneous reactions of this type are extremely complex, usually involving the actual chemical reaction complicated by diffusion and adsorptive effects. In Part II, dealing with the kinetics of the reaction in organic media, the mechanism is further discussed.

The logarithms of the velocity constants of the reaction both for low concentrations of potassium iodide, where the cuprous iodide film is formed, and for higher concentrations of iodide (no film) have been plotted against the reciprocal of the absolute temperature and excellent straight lines are obtained in both cases. From the slopes of these, the critical increment has been calculated; for low concentrations of potassium iodide (4 times that of the initial concentration of iodine in each case) it is 6500 cals./g.-atom of iodine. At higher concentrations of potassium iodide (400 g./l.) the value is 5760 cals. This is in fair agreement with the

value calculated by Moelwyn-Hughes (" Kinetics of Reactions in Solution," p. 279) from Van Name's data, *viz.*, 4040 cals.

The authors thank the Chemical Society for a grant, and one of them (M. H. E.) is indebted to the Governing Body of University College, Exeter, for a grant from the Andrew Simons Fund.

WASHINGTON SINGER LABORATORY, UNIVERSITY COLLEGE, EXETER. [*Received, October 29th*, 1941.]

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124. *Alkyl–Oxygen Fission in Carboxylic Esters. Part II. Derivatives of* p-*Methoxybenzhydrol.*

By MICHAEL P. BALFE, MARK A. DOUGHTY, JOSEPH KENYON, and REGINALD POPLETT.

p-Methoxybenzhydrol, its esters, and ethers undergo a remarkable variety of interconversions when treated with various carboxylic acids or alcohols in excess. Many of its derivatives in which an alkyl–oxygen bond is present give *p*-methoxybenzhydryl chloride when triturated with cold concentrated hydrochloric acid. That alkyl–oxygen fission takes place in these reactions is demonstrated either by the constitution of the products or by the occurrence of racemisation when the reacting compound is optically active.

Alkyl–oxygen fission is also involved in two new reactions of *p*-methoxybenzhydryl hydrogen phthalate. One is the formation of p-*tolyl*-p-*methoxybenzhydrylsulphone* when sodium *p*-toluenesulphinate is added to an aqueous solution of sodium *p*-methoxybenzhydryl phthalate. The second is the separation of the neutral ester from a solution of the hydrogen phthalate in an equimolecular proportion of aqueous sodium hydroxide. It is suggested that the initial stage in both these reactions is ionic alkyl–oxygen fission of the hydrogen phthalate, with racemisation of the resulting *p*-methoxybenzhydryl kation, which then undergoes reaction to give the products in question. Some aspects of the mechanism of the formation of the neutral ester, however, remain obscure.

The preparation of (+)-*p*-methoxybenzhydrol is described.

ALKYL–OXYGEN fission, which is facilitated by increase in the electron-releasing properties of the alkyl group,* can be observed in derivatives of phenylmethylcarbinol and even more readily in those of anisylmethylcarbinol (a communication on these experiments is in preparation); in derivatives of *p*-methoxybenzhydrol it occurs with great ease.

The tendency towards racemisation during the alkaline hydrolysis of hydrogen phthalic esters of some types of optically active alcohols affords an indication of the readiness of esters of these alcohols to react by alkyl–oxygen fission. Some racemisation occurs when dilute alkali is used for hydrolysis of esters of substituted allyl alcohols (Part I, this vol., p. 556), but retention of optical purity is complete (acyl–oxygen fission) when 5N-aqueous sodium hydroxide is employed.

The hydrolysis of (+)-p-*methoxybenzhydryl hydrogen phthalate* even by 10N-aqueous sodium hydroxide results in extensive racemisation; the alcohol of highest rotatory power was obtained when hydrolysis was carried out in ethyl alcohol containing about 2% of water. When the solvent contains 20% of water the hydrolysis is accompanied by much racemisation. The rotatory powers of (+)-*p*-methoxybenzhydrol and its hydrogen phthalate are given in Table I.

TABLE I.

Specific rotatory powers of p-*methoxybenzhydrol and its hydrogen phthalate* (l = 2).

Substance.	Solvent.	*c*, %.	Temp.	$[\alpha]_{6438}$.	$[\alpha]_{5893}$.	$[\alpha]_{5780}$.	$[\alpha]_{5461}$.	$[\alpha]_{4358}$.
Hydrol	CS_2	2·420	13·5°	+38·2°	+47·85°	+49·1°	+59·0°	+120·7°
Acid ester	C_6H_6	2·487	17	+42·5	+52·3	+52·7	+61·9	+119·7
	$CHCl_3$	2·055	18·5	+31·6	+37·0	+35·0	+43·1	+ 78·4
	CH_3OH	2·500	17	—	+28·0	—	—	—
	CS_2	0·340	19	+62·7	+71·2	—	—	—

The ease with which alkyl–oxygen fission occurs in *p*-methoxybenzhydrol and its derivatives is indicated by the readiness of formation of *p*-methoxybenzhydryl chloride, on trituration with cold concentrated hydrochloric acid, not only from the alcohol but also from its esters and ethers. The (+)alcohol and the (−)hydrogen phthalate give the *dl*-chloride, which has also been obtained by this method from the dl-*acetate*, *-benzoate*, and *-methyl ether* and from *dl-p*-methoxybenzhydryl ether. The *dl*-chloride is also obtained by the action of acetyl chloride, at room temperature or on gentle warming, on (+)-*p*-methoxybenzhydrol, *dl-p*-methoxybenzhydryl acetate, and *dl-p*-methoxybenzhydryl ether; these reactions all involve alkyl–oxygen fission.

The reaction of the alcohol with acetyl chloride is a notable example of its tendency to undergo alkyl–oxygen fission, the carbonium kation combining with anionic chlorine. In the more common type of reaction—

* The experiments of Chattaway (J., 1936, 355) form an interesting contrast with those described in the present series of papers. Whereas esters of, *e.g.*, aliphatic alcohols react with ammonia to give the acid amide and the alcohol, Chattaway found that γγγ-trichloro-α-nitro-β-acetoxypropane on treatment with ammonia yields ammonium acetate and γγγ-trichloro-α-nitro-β-aminopropane. The α- and γ-electron-attracting substituents impose so strong a positive charge on the carbinol carbon atom that the unshared electrons of the nitrogen atom in the ammonia are attracted to this carbon atom rather than to the >C=O carbon atom of the acid residue. This mechanism involves alkyl–oxygen fission, but not by the unimolecular mechanism, involving racemisation, which characterises the reactions which we are now discussing. A bimolecular mechanism, involving inversion of configuration, if the carbinol carbon atom were optically active, seems more probable.

acetylation—a proton is separated from an alkoxy-residue and the carbon–oxygen bond is not disturbed. *p*-Methoxybenzhydrol reacts with acetyl chloride by the latter mechanism in the presence of pyridine, yielding the acetate, which indicates that, as suggested by Gerrard (J., 1940, 218), the function of the pyridine in such reactions is to promote removal of the proton from the hydroxyl group, rather than to cause ionic fission of the acid chloride.

The chloride itself undergoes typical reactions of halides with unusual readiness. At room temperature water affords *p*-methoxybenzhydryl ether and a small proportion of the alcohol, sodium hydroxide gives the alcohol, potassium hydrogen phthalate gives the hydrogen phthalic ester, and the hydrol in presence of pyridine yields *p*-methoxybenzhydryl ether. Optically active *p*-methoxybenzhydryl chloride could not be prepared, presumably because of the lability of the chlorine atom. Treatment of the (+)alcohol with thionyl chloride and pyridine, one of the most reliable procedures for preparing optically active chlorides from secondary alcohols, gives a racemic chloride in this case.

(—)-*p*-Methoxybenzhydryl hydrogen phthalate on warming with methyl alcohol yields readily and quantitatively *dl*-*p*-methoxybenzhydryl methyl ether : the racemisation is clear evidence that alkyl–oxygen fission occurs. *dl*-*p*-Methoxybenzhydrol and its normal phthalate also yield the methyl ether on heating with methyl alcohol, presumably by the same mechanism. Similarly, the methyl ether and the benzoate of *dl*-*p*-methoxybenzhydrol yield the acetate when warmed with glacial acetic acid. On the other hand, *p*-methoxybenzhydryl ether does not react when heated with acetic acid or acetic anhydride.

The reactions of *p*-methoxybenzhydryl esters and ethers have not been exhaustively studied, but the examples given above indicate that almost any one of these may be converted into another by treatment with an excess of the appropriate reagent. The alkyl–oxygen bond is so weak that the course of the reactions is controlled by the relative concentrations of the reactants and by phase considerations (separation of insoluble products) rather than by considerations of bond strength.

Optically active *p*-methoxybenzhydrol becomes racemised, without undergoing chemical decomposition, when heated in water, a result which again indicates alkyl–oxygen fission. Its combination with phthalic anhydride in the presence of pyridine—no combination occurs in its absence—results in little, if any, racemisation, indicating that this reaction occurs by the mechanism corresponding to acyl–oxygen fission. The hydrogen phthalate of optically active *p*-methoxybenzhydrol, like that of $\alpha\gamma$-dimethylallyl alcohol (Part I, *loc. cit.*), undergoes racemisation in solvents with which it reacts (acetic acid and methyl alcohol) and in nitromethane solution, and also in solution in benzene in which the hydrogen phthalate of $\alpha\gamma$-dimethylallyl alcohol is optically stable.

Sodium (—)-*p*-methoxybenzhydryl phthalate reacts in aqueous solution with sodium *p*-toluenesulphinate, yielding dl-p-*tolyl*-p-*methoxybenzhydrylsulphone*. The carbon–sulphur is stronger than the carbon–oxygen bond, and the sulphone can be recovered unchanged from hot glacial acetic acid or after heating with concentrated hydrochloric acid. The irreversible formation of the carbon–sulphur bond appears to be the underlying cause of the formation of the sulphone, since from sodium *p*-methoxybenzhydryl phthalate and sodium benzoate (1 mol.) in aqueous solution the neutral phthalic ester (see below) and not *p*-methoxybenzhydryl benzoate is formed. In the reaction with sodium benzoate an equilibrium presumably exists between the hydrogen phthalate and the benzoate of *p*-methoxybenzhydrol.

The reaction with sodium *p*-toluenesulphinate (1 mol.) appears to be characteristic of esters which undergo alkyl–oxygen fission very readily. *Sulphones* are also obtained under these conditions from the hydrogen phthalates of anisylmethylcarbinol and of benzhydrol but not from those of $\alpha\gamma$-dimethylallyl alcohol or phenylmethylcarbinol, though both the latter compounds undergo this type of fission in certain circumstances. The hydrogen phthalates of the *tert.*-alcohol phenylmethylethylcarbinol or of octan-2-ol also do not yield sulphones by this method, nor does the methyl ether of *p*-methoxybenzhydrol on heating under reflux in methyl-alcoholic solution with sodium *p*-toluenesulphinate.

In unpublished experiments with anisylmethylcarbinol, Dr. K. Nandi observed that its hydrogen phthalate, on treatment with dilute aqueous alkali, gave the neutral phthalate. Similar observations have been made with (+)-*p*-methoxybenzhydryl hydrogen phthalate : when this ester is dissolved in 0·15N-sodium hydroxide (1 mol.), separation of an oil begins within a few minutes and is complete after 18 hours, the aqueous solution containing only sodium phthalate. The oil can be separated into *p*-methoxybenzhydrol of low dextrorotation and dextrorotatory di-*p*-methoxybenzhydryl phthalate. Hydrolysis of this neutral ester with alcoholic sodium hydroxide gives dextrorotatory *p*-methoxybenzhydrol with approximately half the rotatory power of the optically pure alcohol. From a solution of (+)-*p*-methoxybenzhydryl hydrogen phthalate and potassium hydrogen phthalate (5 mols.) in 0·3N-sodium hydroxide (1 mol.), a similar oil separates, but in this case both the alcohol and the neutral ester isolated from it are optically inactive.

Our interpretation of these results is that, in the absence of added anions, ionic fission of the acid phthalate ion produces a racemised *p*-methoxybenzhydryl kation. This combines with a second *p*-methoxybenzhydryl phthalate anion to yield the neutral ester, which is insoluble in the aqueous medium. The neutral ester contains one *p*-methoxybenzhydryl radical which has been racemised during its migration, and one which, not having been detached from the phthalate radical, retains its optical purity. Therefore, the alcohol obtained by hydrolysis of the neutral ester possesses half the maximum rotatory power of (+)-*p*-methoxybenzhydrol. Along with the neutral ester some almost racemic alcohol is deposited, formed by interaction of *p*-methoxybenzhydryl kations with hydroxyl ions or water molecules of the solvent. (It appears that the neutral ester

continues to change after its deposition because, when it is left in contact with the supernatant aqueous layer for 12 days before being separated, the proportion of free alcohol present increases, while the alcohol obtained by hydrolysis of the ester is optically inactive.) When phthalate ions are present in excess, most of the liberated kations combine with them to yield racemic *p*-methoxybenzhydryl hydrogen phthalate. From this in turn a neutral ester is slowly formed which on hydrolysis yields a racemic alcohol because both its *p*-methoxybenzhydryl radicals have been through a phase of ionic fission involving their racemisation.

It appears that the formation of the neutral ester is a rapid process. When the hydrogen phthalate is dissolved in aqueous sodium hydroxide (1 mol.) as described above, and the solution kept for 10 minutes before sodium *p*-toluenesulphinate is added, very little sulphone (which is the major product when phthalate and sulphinate solutions are mixed immediately) is formed, the bulk of the acid ester being in this case converted into the neutral ester. The mechanism of formation of the neutral ester is, however, not completely elucidated. The explanation suggested above implies that it involves an intermolecular rearrangement and is supported by the formation of *p*-tolyl-*p*-methoxybenzhydrylsulphone when sodium *p*-toluenesulphinate is added to a freshly prepared solution of the hydrogen phthalic ester in aqueous sodium hydroxide (1 mol.).

However, when the rearrangement occurs in the presence of an excess of octyl hydrogen phthalate (even when the octyl and the *p*-methoxybenzhydryl hydrogen phthalates are dissolved together in the aqueous alkali), the octyl ester does not take part in the reaction and is recovered unchanged from the solution. The product of the reaction is di-*p*-methoxybenzhydryl phthalate, a result which would appear to be inconsistent with an intermolecular mechanism, and on hydrolysis it yields racemic *p*-methoxybenzhydrol, in contrast to the production of a partially active alcohol when the reaction is carried out in the absence of octyl hydrogen phthalate, as described above.

Further, the hydrogen phthalates of phenylmethylcarbinol, γ-phenyl-α-methylallyl alcohol, and benzhydrol when dissolved in equimolecular proportions of aqueous sodium hydroxide remain unchanged; when the solutions are heated, the corresponding alcohols are liberated. On the other hand, all three hydrogen phthalates are known to be capable of undergoing reactions involving alkyl–oxygen fission. The tendency to this type of reaction is greater in derivatives of *p*-methoxybenzhydrol, but it is not obvious how, on this fact alone, an explanation of the complete absence of neutral ester formation from the less reactive hydrogen phthalic esters can be based.

Experimental.

p-Methoxybenzhydrol was prepared by the addition during 6 hours of an ethereal solution of anisaldehyde (122 g., 0·9 mol.) to a Grignard reagent (prepared from bromobenzene, 157 g.), cooling in ice, and decomposing the solid addition compound with ice and ammonium chloride. The dried ethereal extract, evaporated below 60° to small bulk and diluted with light petroleum, deposited the carbinol (150 g.; 78%) in bulky masses of short needles, m. p. 63—65°. After recrystallisation from ether–light petroleum, it separated in rosettes of transparent, prismatic rods, m. p. 66—67° (Adams, Wirth, and French, *J. Amer. Chem. Soc.*, 1918, **40**, 430, give m. p. 68°). In acetic acid solution, chromic acid smoothly oxidised it to *p*-methoxybenzophenone, glassy, prismatic rods, m. p. 61—62°.

dl-p-*Methoxybenzhydryl Hydrogen Phthalate.*—A mixture of the alcohol (10·7 g.), phthalic anhydride (7·5 g.), and pyridine (7 g.) was kept at 55—60° for 4—5 hours. The resulting viscous liquid was diluted with an equal volume of acetone and decomposed with a slight excess of cold dilute hydrochloric acid; the precipitated pasty solid rapidly hardened, and after an hour the resulting crystalline acid *ester* was collected and dried (18·0 g.), m. p. 98—99°. It separated from carbon disulphide in bulky masses of short needles, m. p. 102—103° (decomp.) (Found, on rapid titration with 0·1N-NaOH: *M*, 365. $C_{22}H_{18}O_5$ requires *M*, 362).

Equimolecular amounts of the carbinol (5·3 g.) and phthalic anhydride (3·7 g.) were kept at 120—130° for 4 hours, during which phthalic acid (0·6 g.) separated. No acid phthalic ester was formed under these conditions; the only compound, other than unchanged material, to be isolated was *p*-methoxybenzhydryl ether.

(+)-p-*Methoxybenzhydryl Hydrogen Phthalate.*—A solution of the *dl*-ester (143 g.) and cinchonidine (96·6 g.) in acetone (250 c.c.) after standing overnight deposited the cinchonidine salt of the dextrorotatory hydrogen phthalate. This, after three recrystallisations from ethyl acetate, yielded cinchonidine (+)-*p*-methoxybenzhydryl phthalate (87 g.), bulky clusters of short needles, m. p. 143—144° (decomp.). This salt, mixed with about twice its weight of acetone, was then decomposed with cold dilute hydrochloric acid, and the resulting (+)-p-*methoxybenzhydryl hydrogen phthalate* precipitated by addition of water. It separates from carbon disulphide in bulky clusters of short needles, m. p. 103—103·5° (Found, by rapid titration with 0·1N-NaOH: *M*, 365). Rotatory powers are in Table I.

(+)-p-*Methoxybenzhydrol.*—To a solution of the (+)acid ester (1·81 g.) in cold absolute ethanol (100 c.c.) was added sodium hydroxide (0·9 c.c. of 50%), and the whole heated rapidly on the steam-bath; after 3 mins. a bulky precipitate of sodium hydrogen phthalate had separated. Addition of water resulted in a clear solution from which, on dilution with 3 vols. of water, (+)-*p*-methoxybenzhydrol separated in bulky masses of long, hairy needles (1·05 g.), m. p. 58—59°. Rotatory powers are in Table I. Unless the water content of the alcoholic sodium hydroxide is kept low, racemisation occurs; *e.g.*, in a similar experiment where 10 c.c. of absolute alcohol and 2·5 c.c. of 5N-sodium hydroxide were employed, the resulting *p*-methoxybenzhydrol had only $[\alpha]_{5893}$ +9·4° in carbon disulphide solution.

Hydrolysis of (−)-p-*Methoxybenzhydryl Hydrogen Phthalate with Concentrated Aqueous Sodium Hydroxide.*—The ester (5·4 g., $[\alpha]_{5893}$ −10·2° in benzene) was triturated with sodium hydroxide solution (30 c.c. of 5N); a pasty solid separated which was largely the carbinol, since it dissolved readily in cold methyl alcohol (in which the neutral ester is but sparingly soluble). It was freed from traces of neutral ester by heating the methyl-alcoholic solution after adding a few drops of 50% aqueous sodium hydroxide. The resulting (−)-*p*-methoxybenzhydrol, m. p. 58—61°, had $[\alpha]_{5893}$ −5·5° in carbon disulphide. A second specimen of the hydrogen phthalate ($[\alpha]_{5893}$ −11·6°) was hydrolysed in alcoholic solution (60 c.c.) containing sodium hydroxide (8 c.c. of 5N). The resulting (−)-*p*-methoxybenzhydrol (3·1 g., m. p. 60—62°) had $[\alpha]_{5893}$ −10·4° in carbon disulphide.

A comparison of these two results suggests that the production of the alcohol in concentrated aqueous alkali is the result of two consecutive reactions: (i) conversion of the acid phthalate into the half racemised neutral phthalate; (ii) rapid hydrolysis of the latter.

When 1·8 g. of the (+)phthalate were hydrolysed with 2·5 c.c. of 5N-sodium hydroxide in 10 c.c. of 98% ethyl alcohol, the resulting *p*-methoxybenzhydrol had $[\alpha]^{18°}_{5893}$ +9·4° (*c*, 2·5; *l*, 2) in carbon disulphide solution.

Conversion of (+)-p-*Methoxybenzhydrol into its* (+)*Hydrogen Phthalate.*—The hydrol (0·8 g.; $[\alpha]_{5893}$ +46·8° in carbon disulphide) obtained by hydrolysis in alcoholic solution of its hydrogen phthalate ($[\alpha]_{5893}$ +44·5° in benzene) was heated with phthalic anhydride (0·57 g.) and pyridine (0·6 g.) for an hour at 50—60°. The resulting *p*-methoxybenzhydryl hydrogen phthalate (0·8 g.) had $[\alpha]_{5893}$ +38·4° in benzene solution.

Racemisation of (+)-p-*Methoxybenzhydrol in Hot Aqueous Solution.*—The hydrol (0·56 g.; $[\alpha]_{5893}$ +17·4° in carbon disulphide) was heated with distilled water (750 c.c.) on the steam-bath, and its rotatory power determined at intervals:

Time of heating, hrs.	0	0·5	10	30
$[\alpha]_{5893}$ in CS_2	+17·4°	14·2°	7·0°	0·00°

The resulting *dl-p*-methoxybenzhydrol melted sharply at 65—66°. In a separate experiment the *dl*-alcohol (1 g.) was heated with distilled water (500 c.c.) on the steam-bath for over 100 hours, but was recovered unchanged, m. p. 66°.

Racemisation of (+)-p-*Methoxybenzhydryl Hydrogen Phthalate in Various Solvents at Room Temperature.*—A specimen of the ester had $[\alpha]_{5893}$ +44·5° (*c*, 1·75; *l*, 2) in absolute ethyl alcohol immediately after dissolution; the solution was optically inactive when examined 2 months later. Another specimen of the ester ($[\alpha]_{5893}$ −15·7° in benzene) had $[\alpha]_{5893}$ −2·8° (*c*, 1·0; *l*, 2) in glacial acetic acid when freshly dissolved; after 24 hours the solution was optically inactive. Other observations are given in Table II. From all the solutions referred to in this paragraph phthalic acid was eventually deposited.

TABLE II.

Solvent (*l*, 2)	Methyl alcohol.		Nitromethane.		Benzene.	
c (g./100 c.c.)	2·50		1·3		2·55	
Time, hrs.	$[\alpha]_{5893}$.	Time, hrs.	$[\alpha]_{5893}$.	Time, hrs.	$[\alpha]_{5893}$.	Time, hrs.	$[\alpha]_{5893}$.
0	+28·0°	169	3·4°	0	+17·7°	0	+38·4°	216	14·0°
24	21·8	192	2·2	2	11·5	48	35·8	264	13·4
48	17·2	216	1·6	3	7·7	72	32·0	288	11·0
72	13·1	240	1·1	8	4·2	96	28·2	336	8·8
120	7·6	288	0	19	0	120	26·4	456	6·8
144	6·0					144	22·4	528	6·4
						168	21·4	912	4·4
						192	18·4	1656	1·8

Reaction of p-*Methoxybenzhydryl Hydrogen Phthalate with Acetic Acid.*—The ester (3 g.; $[\alpha]_{5893}$ +45·4° in benzene; *c*, 2·5) was dissolved in glacial acetic acid (60 c.c.); the solution had $\alpha^{18°}_{5893}$ + 2·96° (*l*, 2). After 5 hours the solution, which then had $\alpha^{18°}_{5893}$ +1·47° (*l*, 2), was poured into water, and the oil which separated was extracted with ether. Extraction of the ethereal solution with dilute ammonia yielded the hydrogen phthalate (1·3 g.) with $[\alpha]_{5893}$ +35·0° (*c*, 4·88; *l*, 2) in benzene. Evaporation of the washed ethereal solution yielded *p*-methoxybenzhydryl acetate (0·5 g.), b. p. 190—195°/20 mm.

p-*Methoxybenzhydryl Chloride.*—A. *Preparation by means of concentrated aqueous hydrochloric acid.* (i) From *dl-p*-methoxybenzhydrol. The *dl*-alcohol (2 g.), triturated with hydrochloric acid (10 c.c.), rapidly changed into a liquid which, in turn, soon set to a crystalline powder; this was filtered off, washed with hydrochloric acid, and dried in a vacuum over quicklime (2 g., m. p. 59—60°). Recrystallisation from light petroleum gave *dl-p*-methoxybenzhydryl chloride in bulky clusters of soft, long needles, m. p. 62—63°. When 0·2708 g., dissolved in alcohol (10 c.c.), was warmed for a few minutes with an excess of 0·1N-sodium hydroxide, it neutralised 11·65 c.c. of the alkali (Equiv., 232. Calc.: 232·5) (Bartlett and Nebel, *J. Amer. Chem. Soc.*, 1940, **62**, 1345, who prepared this compound by the action of hydrogen chloride on the alcohol, give m. p. 62—63°).

(ii) From (+)-*p*-methoxybenzhydrol. A specimen of the (+)alcohol (0·50 g.; $[\alpha]_{5893}$ +17·4° in carbon disulphide) was triturated with hydrochloric acid (5 c.c.) as described in (i); the resulting chloride (0·54 g.) without further crystallisation had m. p. 62—63° and was optically inactive in carbon disulphide solution (*c*, 2·5; *l*, 2).

(iii) From *dl-p*-methoxybenzhydryl hydrogen phthalate. When the *dl*-ester (3·62 g.) was triturated with hydrochloric acid (10 c.c.) its crystalline character underwent an immediate change and the temperature of the mixture rose slightly. After 10 mins.' trituration the solid (3·95 g.) was filtered off, washed with hydrochloric acid, and dried. It was separated by extraction with boiling light petroleum into phthalic acid (1·60 g.; calc., 1·66 g.) and *p*-methoxybenzhydryl chloride (m. p. 62—63°; 2·20 g.; calc., 2·32 g.).

(iv) From (−)-*p*-methoxybenzhydryl hydrogen phthalate. A specimen of the (−)ester (1·81 g., $[\alpha]_{5893}$ −18·2° in benzene), treated with hydrochloric acid (5 c.c.) as in (iii), yielded phthalic acid (0·81 g.) and *dl*-p-methoxybenzhydryl chloride (m. p. 61—62°, 1·10 g.) which was optically inactive in carbon disulphide solution (*c*, 2·5; *l*, 2).

(v) From *dl-p*-methoxybenzhydryl acetate. The acetate (0·5 g.), triturated with hydrochloric acid (2 c.c.), gradually changed into a crystalline solid, m. p. 57—59°. This separated from light petroleum in bulky clusters of fine needles (0·3 g.), m. p. 62—63° alone or when mixed with authentic *p*-methoxybenzhydryl chloride.

(vi) From *dl-p*-methoxybenzhydryl ether of m. p. 120°. The finely powdered ether (1·00 g.) was triturated with hydrochloric acid (6 c.c.), and the mixture warmed to about 50° for a few minutes until the crystals melted. On cooling, the molten liquid set at once to a hard crystalline mass (1·15 g.; calc., 1·16 g.); after being powdered and dried, it had m. p. 62—63° alone or mixed with an authentic specimen of *p*-methoxybenzhydryl chloride. This reaction proceeds immediately at room temperature, but unless the reaction product is warmed the crystals of ether become coated with a protecting layer of *p*-methoxybenzhydryl chloride.

(vii) From *p*-methoxybenzhydryl methyl ether. This ether (0·4 g.) was triturated in concentrated hydrochloric acid (2 c.c.). An oil formed which rapidly solidified. This chloride (0·35 g.) separated from light petroleum in needles, m. p. 61—62°; mixed m. p. 62—63°.

(viii) From *p*-methoxybenzhydryl benzoate. The ester (1 g.) was triturated with concentrated hydrochloric acid (1 c.c.). The dried product (1·1 g.) separated from light petroleum in small needles, m. p. 60—61°; mixed m. p. with an authentic specimen of *p*-methoxybenzhydryl chloride, 62—63°. Benzoic acid was recovered from the light petroleum filtrates.

B. *Preparation by means of acetyl chloride.* (i) From *dl-p*-methoxybenzhydrol. The *dl*-alcohol (1·0 g.) dissolved readily in acetyl chloride (1 c.c.) with some evolution of heat, but not of hydrogen chloride, and the solution rapidly became semi-solid. The product, after standing overnight in an evacuated desiccator containing sodium hydroxide, had m. p. 60—61° and separated from light petroleum in needles, m. p. 62—63° (1·0 g.) alone or mixed with authentic *p*-methoxybenzhydryl chloride. It is clear that no significant amount of acetylation had occurred.

(ii) From (+)-*p*-methoxybenzhydrol. When experiment (i) was repeated upon a carbinol (0·5 g.) with $[\alpha]_{5893}$ +17·4°

in carbon disulphide, the resulting *dl-p*-methoxybenzhydryl chloride (0·55 g.) was optically inactive in carbon disulphide solution (*c*, 2·5; *l*, 2).

(iii) From *dl-p*-methoxybenzhydryl ether. The powdered ether (1·0 g.) dissolved rapidly in warm acetyl chloride (1 c.c.) and the solution at once set to a crystalline mass. After standing in a vacuum over sodium hydroxide for 2 days the resulting dry powder was completely soluble in hot light petroleum, and separated therefrom on cooling in needles (1·0 g.), m. p. 62—63°, alone or mixed with authentic *p*-methoxybenzhydryl chloride.

(iv) From *dl-p*-methoxybenzhydryl acetate. A solution of the acetate (0·5 c.c.) in cold acetyl chloride (1 c.c.) was placed in a desiccator containing sodium hydroxide. Next day, the solid residue was crystallised from light petroleum, needles (0·3 g.), m. p. 62—63°, of *p*-methoxybenzhydryl chloride being obtained.

C. *Preparation by means of thionyl chloride and pyridine.* Thionyl chloride (0·65 g.) was added slowly to an ice-cold solution of *p*-methoxybenzhydrol (1·07 g., $[\alpha]_{5893}$ +29·0° in carbon disulphide) in pyridine (0·40 g.). After a vigorous reaction, the whole set solid within 5 minutes. Extraction with warm, light petroleum removed the chloride. The first crop (m. p. 60—61°; 0·12 g.) was optically inactive in carbon disulphide (*c*, 2·40; *l*, 1).

Reactions of dl-p-*Methoxybenzhydryl Chloride.*—(i) *With cold water.* A solution of the chloride (0·8 g.) in ether (25 c.c.) was shaken with water three times: the first two washings were acid to Congo-red but the third was not. The dried ethereal solution deposited glassy rhombs of *p*-methoxybenzhydryl ether (0·5 g.), m. p. 119—120°; a small second crop (needles, m. p. 55—60°) consisted probably of *p*-methoxybenzhydrol mixed with traces of the ether.

(ii) *With sodium hydroxide.* Sodium hydroxide (2 c.c. of 3N) was added to a solution of the chloride (0·8 g.) in acetone (5 c.c.). After an hour, addition of water precipitated an oil which rapidly set to a mass of crystalline plates. These (0·7 g.) had m. p. 65—66°, alone or mixed with authentic *p*-methoxybenzhydrol.

(iii) *With potassium hydrogen phthalate.* The finely powdered salt (1·02 g.) was added to a solution of *p*-methoxybenzhydryl chloride (1·17 g.) in dry acetone (15 c.c.), and the gently warmed suspension triturated at intervals during 3 hours. The reaction mixture was diluted with water, extracted with ether, and the ethereal solution extracted with dilute ammonia. Addition of hydrochloric acid to the alkaline extract precipitated *p*-methoxybenzhydryl hydrogen phthalate as a fine crystalline powder (1·1 g.), m. p. 98—99° alone or mixed with a specimen prepared directly from the alcohol.

(iv) *With* dl-p-*methoxybenzhydrol.* A few drops of pyridine were added to a solution of *p*-methoxybenzhydryl chloride (0·23 g.) and *p*-methoxybenzhydrol (0·21 g.) in dry ether. Next day the solution was washed with dilute acid, dried, and evaporated. Crystallisation of the residue from acetone yielded *p*-methoxybenzhydryl ether (0·3 g.) in glassy rhombs, m. p. 119—120°.

Preparation of dl-p-*Methoxybenzhydryl Acetate.*—(i) A mixture of the *dl*-alcohol (5·3 g.), acetic anhydride (3 g.), and pyridine (2 g.), after standing for 2 days at room temperature, was dissolved in ether, and the solution washed successively with dilute acid, sodium carbonate, and water. The resulting dl-p-*methoxybenzhydryl acetate* (5 c.c.) had b. p. 182—183°/4 mm. (0·3548 G. on hydrolysis with 0·1N-sodium hydroxide, neutralised 13·90 c.c. $C_{16}H_{16}O_3$ requires 13·85 c.c.). It showed no tendency to crystallise when kept in a refrigerator for several weeks.

(ii) Acetyl chloride (2 g.) was added dropwise to a mixture of the *dl*-alcohol (5·3 g.) and pyridine (2 g.) cooled in ice, and the mixture warmed for 30 minutes. The product was decomposed with ice, extracted with ether, and washed as before; b. p. 168—170°/2 mm., $n_D^{10°}$ 1·5649.

(iii) A mixture of the *dl*-alcohol (4 g.) and acetic anhydride (2 g.) was heated on the steam-bath for 3 hours and worked up. The main product had b. p. 172—173/3 mm., $n_D^{10°}$ 1·5672. An undistilled residue (about 1 g.) separated from methyl alcohol in small rhombs (0·5 g.), m. p. 119—120° alone or mixed with *p*-methoxybenzhydryl ether.

(iv) *dl-p*-Methoxybenzhydrol (3 g.) in acetic anhydride (10 c.c.) was heated for 3 hours on a steam-bath. Direct distillation gave the acetate (3 c.c.), b. p. 185—186°/5 mm., $n_D^{10°}$ 1·5640.

(v) A solution of (+)-*p*-methoxybenzhydrol in acetic acid after being heated on the steam-bath for 5 hours was optically inactive.

(vi) A solution of *dl-p*-methoxybenzhydryl methyl ether (2 g.) in glacial acetic acid (30 c.c.) was heated for 6 hours, and the acetic acid distilled off. The residue had b. p. 210°/20 mm. (1·5 g.) and was shown to be *p*-methoxybenzhydryl acetate by hydrolysis to sodium acetate and *p*-methoxybenzhydrol (1·1 g.), m. p. 64—65°.

p-*Methoxybenzhydryl Benzoate.*—(i) Benzoyl chloride (6·4 g.) was slowly added to an ice-cold solution of *p*-methoxybenzhydrol (8·56 g.) in pyridine (4 c.c.), and the mixture warmed for 0·5 hour at 50—60°. Decomposition with ice-cold dilute hydrochloric acid gave a solid *benzoate* (8·3 g.); this separated from ethyl alcohol in clusters of small needles, m. p. 57—58° (Found: C, 79·1; H, 5·8. $C_{21}H_{18}O_3$ requires C, 79·2; H, 5·7%).

(ii) *p*-Methoxybenzhydrol (2·14 g.) was converted into its chloride and dissolved in acetone (20 c.c.). Sodium benzoate (1·44 g.) in water (10 c.c.) was added, giving an immediate precipitate of sodium chloride. After several hours, the solution was diluted, depositing an oil, which solidified on cooling. The benzoate separated from ethyl alcohol in small needles, m. p. 58° alone and when mixed with the ester from experiment (i).

p-*Methoxybenzhydryl Ether.*—Recrystallised *p*-methoxybenzhydrol (m. p. 66—67°, 4 g.) distilled at 196—198°/11 mm., leaving a residue (0·5 g.). The distillate set to a hard, crystalline mass, m. p. 67°, of unchanged carbinol. The residue, dissolved in warm ether, yielded crystalline rhombs which, after recrystallisation from ether or alcohol, formed well-defined, rhombic, glassy plates, m. p. 120°, of *p*-methoxybenzhydryl ether (Kohler and Patch, *J. Amer. Chem. Soc.*, 1916, **38**, 121, give m. p. 120°) [Found: C, 81·95; H, 6·35; OMe, 13·9; *M* (Rast), 390. Calc.: C, 81·95; H, 6·34; OMe, 15·1%; *M*, 410]. This compound is unaffected by bromine in carbon tetrachloride solution, by benzoyl chloride and pyridine, by boiling acetic anhydride, or by boiling in water or in methyl alcohol for 92 hours. When, however, the methyl alcohol contained a few drops of sulphuric acid, the ether was quantitatively converted into *p*-methoxybenzhydryl methyl ether (m. p. 26—27°) by 4 hrs.' heating.

Preparation of p-*Methoxybenzhydryl Methyl Ether.*—(i) *From* (−)-p-*methoxybenzhydryl hydrogen phthalate.* A solution of the (−)-ester (7·24 g., $[\alpha]_{5893}$ −2·4° in benzene) in dry methyl alcohol (200 c.c.) was distilled during 2·5 hrs. The residue was separated into phthalic acid (3·3 g.; calc., 3·32 g.) and p-*methoxybenzhydryl methyl ether* (4 c.c.), b. p. 195°/17 mm., m. p. 28—29°. The latter separates from ether–light petroleum in glassy tablets, m. p. 29°. It was optically inactive both in the homogeneous state (*l*, 0·25) and in ethereal solution (*c*, 4·7; *l*, 2) (Found: C, 78·8; H, 7·0. $C_{15}H_{16}O_2$ requires C, 79·0; H, 7·0%).

(ii) *From di*-dl-p-*methoxybenzhydryl phthalate.* After standing in an open vessel for about 20 days, a solution of the ester (2·5 g.) in methyl alcohol (60 c.c.) left a residue, partly crystalline and partly oily. This was completely separated by extraction with cold petrol into phthalic acid and the very soluble *p*-methoxybenzhydryl methyl ether; after evaporation of the solvent, the latter formed glassy, irregular rhombs, m. p. 29° alone and mixed with the specimen prepared in (i).

(iii) *From* dl-p-*methoxybenzhydrol.* A solution of the alcohol (5 g.) in dry methanol (100 c.c.) was slowly distilled during 6 hours, and the oily residue kept in a vacuum for an hour. On inoculation with *p*-methoxybenzhydryl methyl ether it rapidly set to a crystalline mass of glassy, irregular rhombs, m. p. 29° alone and when mixed with the methyl ether prepared in (i). It separated from petrol in rhombs, m. p. 29°.

o-Methoxybenzhydrol (m. p. 35°) and α-naphthylanisylcarbinol (m. p. 88°) do not react with methyl alcohol under these conditions.

Interaction of p-*Methoxybenzhydryl Chloride and Sodium* p-*Toluenesulphinate.*—Solutions of the sulphinate (1 g.) in warm water (4 c.c.) and the chloride (0·78 g.) in acetone (10 c.c.) were mixed, and sufficient acetone added to render the whole homogeneous. Sodium chloride began to separate immediately. After a few minutes water was added, and the resulting clear solution, on further dilution, deposited a crystalline precipitate. This when dried (1·2 g.; calc., 1·18 g.) had m. p. 159—160°; crystallisation from boiling alcohol (120 c.c.) afforded p-*tolyl*-p-*methoxybenzhydrylsulphone* in clusters of prismatic needles, m. p. 160° (Found: S, 8·7. $C_{21}H_{20}O_3S$ requires S, 9·1%). It was recovered unchanged after being heated for several hours on the steam-bath with glacial acetic acid or concentrated hydrochloric acid.

Interaction of (−)-p-*Methoxybenzhydryl Hydrogen Phthalate and Sodium* p-*Toluenesulphinate.*—The phthalate (1·81 g., $[\alpha]_{5893}$ −15·7° in benzene) was rapidly dissolved in sodium hydroxide (18 c.c. of 0·3N), and the solution filtered into a solution of sodium *p*-toluenesulphinate (1·1 g.) in water (25 c.c.); a bulky crystalline precipitate soon began to form, and separation appeared to be complete after some 20 mins. The dried precipitate (1·8 g.), m. p. 159—160°, was optically inactive in chloroform solution (*c*, 5; *l*, 2). It separates from ether or alcohol in clusters of prismatic needles, m. p. 160° alone or mixed with *p*-tolyl-*p*-methoxybenzhydrylsulphone prepared as described above.

If the hydrogen phthalate is dissolved in the sodium hydroxide, and the solution kept for 10 mins. before it is added to the solution of the sulphinate, only a trace of sulphone is formed, but the neutral phthalate is deposited, as in the absence of sodium *p*-toluenesulphinate.

Experiments with Hydrogen Phthalates of Other Alcohols.—Each ester (0·005 mol.) was dissolved in 0·3N-sodium hydroxide (17 c.c.) and filtered into a solution of sodium *p*-toluenesulphinate (1·07 g., 0·005 mol.) in water (15 c.c.), the mixture being left at room temperature. During 4 weeks no deposit separated in the experiments with the hydrogen phthalates of the following alcohols: *m*-methoxybenzhydrol, anisyl alcohol, phenylmethylethylcarbinol, phenylmethylcarbinol, αγ-dimethylallyl alcohol, octan-2-ol. From the hydrogen phthalate of *o*-methoxybenzhydrol, a crystalline deposit separated slowly during 6 days, whereas from that of *p*-methoxybenzhydrol the deposition is complete after 1 hour.

A solution of (−)anisylmethylcarbinyl hydrogen phthalate (3·0 g. of $[\alpha]_{5893}$ −18·0° in ethyl alcohol) in sodium hydroxide (35 c.c. of 0·3N) was filtered into a solution of sodium *p*-toluenesulphinate (2·15 g.) in water (25 c.c.). The solution rapidly turned cloudy and began to deposit a fine crystalline precipitate of p-*tolyl*-α-*anisylethylsulphone*. After a week, this was filtered off, washed, and dried. It (1·6 g.) was optically inactive in chloroform solution. It separates from alcohol as a crystalline powder, m. p. 119—120° (Found: S, 11·0. $C_{16}H_{18}O_3S$ requires S, 11·0%).

To a solution of benzhydryl hydrogen phthalate (1·66 g.) in 0·3N-sodium hydroxide (18 c.c.), sodium *p*-toluenesulphinate (1·07 g.) dissolved in water was added. The solution remained clear after 2 weeks at room temperature. It was then heated on the steam-bath for about 10 hrs. during which a crystalline precipitate (1·30 g.) separated. This p-*tolylbenzhydrylsulphone*, after two crystallisations from ethyl alcohol, had m. p. 190—191°; yield 0·9 g. (Found: S, 10·0. $C_{20}H_{18}O_2S$ requires S, 10·0%).

Action of Dilute Aqueous Sodium Hydroxide on (+)-p-*Methoxybenzhydryl Hydrogen Phthalate.*—A solution of the ester (7·24 g.) in cold sodium hydroxide (280 c.c. of 0·15N) began to turn milky after a few minutes, and after 18 hours, a layer of very viscous oil had separated. The clear supernatant liquid was decanted—a portion neutralised with hydrochloric acid gave no precipitate, showing that the hydrogen phthalate had been completely decomposed—evaporated to small bulk, and acidified; the resulting phthalic acid weighed 2·40 g. The oil was dissolved in ether, and the ethereal solution washed with water, dried, and evaporated. The residue (4·93 g.) was extracted with hot methyl alcohol (15 c.c.), and the whole rapidly cooled; the neutral ester (A) at once separated as an oil (2·73 g.). The decanted methyl-alcoholic extract, diluted with water, yielded crude *p*-methoxybenzhydrol, which was spread on porous earthenware to remove adhering oil. This (1·8 g.) was separated by several crystallisations from carbon disulphide and light petroleum into *p*-methoxybenzhydrol (1·4 g.; $[\alpha]_{5893}$ +3·4° in carbon disulphide) and the oily neutral ester (about 0·2 g.).

The viscous oil (A) had $[\alpha]_{5893}$ +23·5° in carbon disulphide (*c*, 5·0; *l*, 2); it (2·40 g.) was dissolved in warm absolute alcohol, mixed with sodium hydroxide (1 c.c. of 50%), and heated on the steam-bath for 30 mins. On addition of water, the crystalline sodium hydrogen phthalate which had separated dissolved, and the resulting clear solution was diluted with an equal volume of water and left in an open beaker for 2 days. The (+)-*dl*-*p*-methoxybenzhydrol (1·88 g.; calc., 1·85 g.), m. p. 62—63°, which had separated had $[\alpha]_{5893}$ +19·0° in carbon disulphide. The alkaline liquor yielded phthalic acid (0·55 g.; calc., 0·71 g.).

This experiment constitutes an approximate analysis of the neutral ester; the amounts of *p*-methoxybenzhydrol and phthalic acid obtained are in good agreement with the theoretical but suggest that the neutral ester was not completely free from admixed carbinol. It is probable also that the carbinol of $[\alpha]_{5893}$ +3·4° was not completely free from neutral ester; *dl*-*p*-methoxybenzhydrol tends to separate when *d* + *dl*-carbinol is fractionally crystallised from carbon disulphide, so it was not feasible to recrystallise the carbinol further. As these two factors act in opposite directions, it is probable that the rotatory power given is close to the true value.

This experiment was repeated with a hydrogen phthalic ester (7·26 g.) of $[\alpha]_{5893}$ +44·0° and 0·3N-sodium hydroxide. The (+)-*dl*-carbinol obtained had $[\alpha]_{5893}$ +2·4° (*c*, 2·5; *l*, 2) in carbon disulphide; the neutral ester had $[\alpha]_{5893}$ +18·4° and on hydrolysis yielded *p*-methoxybenzhydrol, $[\alpha]_{5893}$ +17·2° (*c*, 2·5; *l*, 2), both in carbon disulphide.

In a similar experiment, using hydrogen phthalate (3·62 g.) of $[\alpha]_{5893}$ −10·0° in benzene, the oil was left in contact with the supernatant water for 12 days. During this time, the proportion of crystalline deposit (*p*-methoxy-benzhydrol) increased. The oil was then separated, hydrolysed as described above, and the solution diluted with water. The alcohol which separated (0·75 g., m. p. 58—63°) was optically inactive in carbon disulphide solution. Phthalic acid (0·6 g.) was recovered on acidifying the alkaline solution after removal of the alcohol.

Action of Dilute Sodium Hydroxide on (−)-p-*Methoxybenzhydryl Hydrogen Phthalate in Presence of Sodium Phthalate.*—A solution of the (−)-hydrogen phthalate (3·69 g., $[\alpha]_{5893}$ −15·7° in benzene) in sodium hydroxide (34 c.c. of 0·3N) was filtered quickly into a solution of potassium hydrogen phthalate (10·2 g.; 5 mols.) in sodium hydroxide (170 c.c. of 0·3N). At the end of 4 hrs., a fibrous, crystalline precipitate was suspended in the liquid and a lower layer of viscous oil had separated. Filtration yielded the crystalline *p*-methoxybenzhydrol (0·45 g.), m. p. 59—62°, mixed m. p. with an authentic specimen, 62—63°; it was optically inactive in carbon disulphide solution. The oily neutral ester, hydrolysed with alcoholic sodium hydroxide, gave the alcohol (1·15 g.), which was optically inactive in carbon disulphide solution.

Action of Dilute Aqueous Sodium Hydroxide on dl-p-*Methoxybenzhydryl Hydrogen Phthalate in Presence of Sodium Benzoate.*—The phthalate (1·81 g., 1 mol.) was dissolved in 0·3N-sodium hydroxide (18 c.c.; 1 mol.), and the solution added to a solution of sodium benzoate (0·7 g., 1 mol.) in water (10 c.c.). Di-*p*-methoxybenzhydryl phthalate separated as an oil, as in the corresponding experiment in the absence of sodium benzoate. Benzoic acid (0·5 g.) was recovered by acidification of the aqueous layer, indicating that the sodium benzoate had not reacted.

Action of Dilute Sodium Hydroxide on (−)-p-*Methoxybenzhydryl Hydrogen Phthalate in Presence of* (+)-β-*Octyl Hydrogen Phthalate.*—(i) A solution of the (−)hydrogen phthalate (3·6 g., $[\alpha]_{5893}$ −15·7°) in sodium hydroxide (34 c.c. of 0·3N) was filtered into a solution of (+)-β-octyl hydrogen phthalate (13·9 g., 5 mols.) in sodium hydroxide (170 c.c. of 0·3N).

The solution soon began to turn cloudy owing to separation of oily globules. After a week the oil was removed by extraction with ether, and then hydrolysed in alcoholic sodium hydroxide solution. The resulting *p*-methoxybenzhydrol (1·76 g.) had m. p. 61—63° and was optically inactive in carbon disulphide solution. The (+)octyl hydrogen phthalate (12·5 g., m. p. 74°) was recovered unchanged.

(ii) (+)-*p*-Methoxybenzhydryl hydrogen phthalate (3·6 g., $[\alpha]_{5893}$ +52·3° in benzene) and (+)octyl hydrogen phthalate (13·9 g.) were dissolved together in sodium hydroxide (205 c.c., 0·3N). From the filtered solution an oil began to separate rapidly; after 18 hrs. it was removed by extraction with ether and hydrolysed with alcoholic sodium hydroxide. The resulting *p*-methoxybenzhydrol (1·4 g., m. p. 58—59°) was optically inactive in carbon disulphide solution. The (+)octyl hydrogen phthalate (12 g.), m. p. 74°, was recovered unchanged, and no octyl alcohol was obtained when the alkaline liquor, from which the *p*-methoxybenzhydrol had been removed, was distilled in a current of steam.

Benzhydryl hydrogen phthalate was prepared by heating a mixture of benzhydrol (7 g.), phthalic anhydride (6 g.), and pyridine (4 g.) at 60—70° for 5 hours. The resultant viscous liquid was diluted with acetone and decomposed with ice-cold dilute hydrochloric acid; the precipitated oily phthalate solidified on standing, and the crystals were filtered off and dried (11 g.). They separated from methylene chloride in small needles, m. p. 157—158°, not raised by further recrystallisation (Fessler and Shriner, *J. Amer. Chem. Soc.*, 1936, **58**, 1385, give m. p. 164—165°) (Found, by titration with sodium hydroxide: *M*, 330. Calc.: *M*, 332).

A solution of *dl*-phenylmethylcarbinyl hydrogen phthalate in 0·3N-sodium hydroxide remained perfectly clear after 5 weeks, and when acidified yielded the unchanged ester.

A solution of benzhydryl hydrogen phthalate (4·05 g.) in sodium hydroxide (45 c.c. of 0·3N) on standing for 2 weeks deposited some crystals of sodium benzhydryl phthalate which redissolved on warming, but otherwise no apparent change occurred. The solution was then heated on the steam-bath for about 10 hours; an oil separated, and on cooling it set to a crystalline mass of benzhydrol (2·2 g.; calc., 2·3 g.), m. p. 58—64°, raised to 65—66° by one crystallisation.

A solution of γ-phenyl-α-methylallyl hydrogen phthalate (2·3 g.) in sodium hydroxide (35 c.c.) after 2 days had deposited an oil and become acidic. A further 10 c.c. of sodium hydroxide was added, and the oil extracted with ether. On inoculation with *dl*-γ-phenyl-α-methylallyl alcohol it set to a crystalline mass, m. p. 29—30°. Acidification of the alkaline liquor yielded phthalic acid (1·3 g.), showing that hydrolysis was complete.

Thanks are due to the Royal Society and to Imperial Chemical Industries, Ltd., for grants.

BATTERSEA POLYTECHNIC, LONDON, S.W.11. [*Received, June 15th*, 1942.]

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125. *The Separation of Diastereoisomerides by Selective Adsorption on Optically Inactive Material.*

By MARGARET M. JAMISON and E. E. TURNER.

Diastereoisomerides should have different coefficients of adsorption on adsorbents devoid of stereo-orientation. It is shown that *l*-menthyl *d*- and *l*-mandelates are adsorbed selectively on alumina.

THERE are two ways in which the technique of the adsorption column could be used to separate the active forms of a racemic substance. The first (Karagunis and Coumoulos, *Praktika*, 1938, **13**, 414; *Nature*, 1938, **142**, 162; Henderson and Rule, J., 1939, 1568) consists in running a solution of the racemic mixture down a column of optically active adsorbent (quartz; lactose). In the second, which corresponds more closely to classical methods of resolution, the racemic substance would be converted into diastereoisomerides by combination with a second purely *d*- or *l*-compound, whereupon selective adsorption might be expected to take place on *non*-asymmetrical material, since the diastereoisomerides should have different coefficients of adsorption. Stoll and Hofmann (*Z. physiol. Chem.*, 1938, **251**, 155), apparently without theoretical justification, attempted to separate the two forms of *dl-iso*lyserg-*d*-β′-hydroxy*iso*propylamide, but the facts that they crystallised and inoculated their chromatographically separated fractions (opening up the possibility of resolution) and that their observed rotations were very small make this an unsatisfactory example for the demonstration of the important fundamental principle, apart from the fact that the constitution of lysergic acid is unknown.

In order to investigate the question we have taken the *l*-menthyl esters of *dl*-mandelic acid, which McKenzie (J., 1904, **85**, 378, 1249) was unable to separate by fractional crystallisation during a thorough search using a large variety of solvents. Alumina (Birlec) was used as adsorption material, and all solvents were purified finally by running them down a column of this material.

The following specific rotations of optically pure compounds were determined in ethyl alcohol for reference:

l-Menthyl *l*-mandelate, m. p. 81—82°, $[\alpha]_{5461}^{19\cdot0°}$ −163·5° (c = 2·3072; l = 2)
l-Menthyl *dl*-mandelate, m. p. 85—86°, $[\alpha]_{5461}^{19\cdot7°}$ −87·3° (c = 1·2485; l = 2)
l-Mandelic acid, m. p. 133°, $[\alpha]_{5461}^{19\cdot5°}$ −184·6° (c = 1·6780; l = 2)

The *l*-mandelic acid was obtained from amygdalin; the esters were prepared according to McKenzie (*loc. cit.*), who also gives the m. p. of *l*-menthyl *d*-mandelate as 99—100°.

EXPERIMENTAL.

In the present work three types of experiment have been carried out, all of which demonstrate that preferential adsorption does occur; an example of each follows.

(1) A solution of 5 g. of *l*-menthyl *dl*-mandelate in 500 c.c. of light petroleum (b. p. 80—100°) was run down a column of alumina (4 ft. × ½ in. diam.), followed by 250 c.c. of the pure solvent. The top 6-in. portion of the column was then completely extracted by a mixture of alcohol and benzene, and the solvent evaporated. The resulting solid residue in

ethyl-alcoholic solution had $\alpha_{5461}^{19.7°}$ −1·10° (c = 0·5492; l = 2), whence $[\alpha]_{5461}^{19.7°}$ = − 100·2°, representing 58·5% of *l*-menthyl *l*-mandelate and 41·5% of *l*-menthyl *d*-mandelate. Total saponification of the product by heating for a short time with aqueous-alcoholic potash gave an acid having $\alpha_{5461}^{19.7°}$ = −0·64°, $[\alpha]_{5461}^{19.7°}$ = −18·2° (c = 1·6660; l = 2). This and all other saponification experiments were carried out using an excess of potash, in order to avoid the possibility of partial saponification giving preferential release of one form of the acid: considerable racemisation is inevitable (see McKenzie, *loc. cit.*). Elution of the fourth 6-in. portion of the column gave an ester having $\alpha_{5461}^{19.7°}$ −0·93° in alcohol (c = 1·4820; l = 2), $[\alpha]_{5461}^{19.7°}$ −31·9° (86·5% of *d*-ester). Saponification gave an acid having $\alpha_{5461}^{19.7°}$ +0·57° (c = 0·4450; l = 2), $[\alpha]_{5461}^{19.7°}$ = + 64·0°.

(2) A solution of 5 g. of *l*-menthyl *dl*-mandelate in 1 l. of light petroleum (b. p. 60—80°) was put through a column of alumina (85 g.) (2 ft. × ½ in. diam.). The column was divided into six equal portions, each eluted with alcohol–light petroleum (b. p. 60—80°) (1 : 1), and the solvent removed by evaporation. The properties of the esters obtained and of the acids they yielded on saponification are tabulated below. The rotations are all measured in ethyl-alcoholic solution.

Esters.

	Weight, g.	M. p.	$\alpha_{5461}^{19.7°}$.	$[\alpha]_{5461}^{19.7°}$.	c, %.	Percentage of *l*-*l*-ester.
1	0·80	82—83°	−0·99°	−99·0°	0·5000	57·5
2	1·00	85—86	−0·95	−95·0	0·5000	55·0
3	0·975	85—86	−0·94	−94·0	0·5000	54·5
4	0·90	85—86	−0·94	−94·0	0·5000	54·5
5	0·70	80—87	−0·54	−54·0	0·5000	28·0
6	0·03	88—92	−0·12	−60·0	0·1000	32·0

Acids.

Sample of ester giving acid.	M. p.	$\alpha_{5461}^{19.7°}$.	$[\alpha]_{5461}^{19.7°}$.	c, %.
1 (above)	115—120°	−0·13°	−13·0°	0·5000
3 + 4	110—117	−0·09	− 9·0	0·5000
5 + 6	105—107	+0·14	+14·0	0·5000

(3) A solution of 5 g. of *l*-menthyl *dl*-mandelate in 250 c.c. of light petroleum (b. p. 60—80°) was run through 68 g. of alumina in a column 2 ft. × 0·45 in. diam. The column was then washed with pure solvent, the filtrate taken off in successive volumes of 250 c.c., each evaporated to dryness, and the residue of ester examined.

Ester from	Weight, g.	M. p.	$\alpha_{5461}^{19.7°}$.	$[\alpha]_{5461}^{19.7°}$.	c.	Percentage of *l*-*l*-ester.
1st portion, 2nd ,, ...	0·52	90—95°	−0·32°	−32·0°	0·5000	14·0
3rd ,, ...	0·33	85—88	−0·57	−57·0	0·5000	30·0
4th ,, ...	0·1	81—82	−0·815	−81·5	0·5000	46·0

Elution of the first 4 in. of the column after this washing gave 0·35 g. of ester having m. p. 81—85°, $\alpha_{5461}^{19.7°}$ − 1·10° (c = 0·5000; l = 2), $[\alpha]_{5641}^{19.7°}$ = − 110·0° (65% of *l*-*l*-ester).

The actual observed angles of rotation are much larger than those of any previously recorded work on the use of adsorption in stereochemistry. Examination of the above results leaves no doubt that the coefficient of adsorption on inactive material can be added to the list of physical properties in which diastereoisomerides can be expected to differ. It is probable that, given a suitable adsorbent, diastereoisomeric *salts* could be separated in this way, and experiments in this direction will be undertaken when circumstances permit.

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c/o THE UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE.

[*Received, June 16th*, 1942.]

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126. *The Mechanism of Additions to Double Bonds. Part XIV.* The Nature of the Activated Complex in Bimolecular Diene Syntheses.*

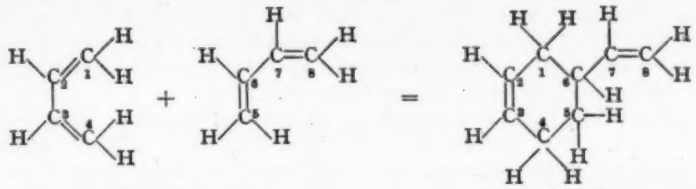
By ALBERT WASSERMANN.

The rate-determining step in the bimolecular dimerisation of gaseous butadiene might involve an activated complex stereochemically similar to (*a*) 4-vinyl*cyclo*hexene or (*b*) an open-chain diradical which is subsequently converted into the cyclic product. In discussing these two possibilities, Kistiakowsky and Ransom concluded that mechanism (*b*) is operative, but it is now shown that this mode of addition is not proved. Attention is directed to the fact that the kinetic course of the association of butadiene and of other bimolecular diene syntheses is not altered by oxygen or peroxides, and this indicates that free radicals do not play a rôle as intermediates. It appears more probable, therefore, that the slowest stage of these processes involves activated complexes of the same stereochemical type as the stable product molecules.

AN attempt is here made to find out whether bimolecular diene syntheses (Diels–Alder reactions) involve activated complexes which are stereochemically similar to the product, or whether the rate-determining step consists in the formation of radicals which are subsequently converted into the stable associated species. The first mode of addition is characterised by bimolecular collisions in which a close contact between the carbon atoms of the reactants occurs at two specified positions, whereas the slowest stage of the alternative mechanism is of such a nature that a close contact between the carbon atoms of the reactants occurs at one point only. In order to decide between these possibilities Kistiakowsky and Ransom (*J. Chem. Physics*, 1939, **7**, 725)

* For Parts XI—XIII, see *Trans. Faraday Soc.*, 1939, **35**, 841, 1022; J., 1940, 735.

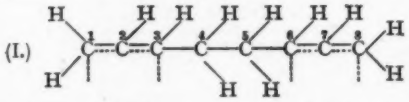
attempted to estimate the entropy of activation of the simplest gaseous diene synthesis, *viz.*, the dimerisation of butadiene :



(1)

Butadiene. 4-Vinyl*cyclo*hexene.

The *a priori* calculation was made on the assumption that the activated complex is stereochemically similar either to (*a*) 4-vinyl*cyclo*hexene or to (*b*) the open-chain diradical (I), and a comparison of the theoretical



(I.)

(The bonds between atoms 1, 2, and 3, and 6, 7, and 8 are assumed to be intermediate between ordinary double and single bonds. The four vertical dotted lines indicate two free valencies. Formation of a bond between the carbon atoms 1 and 6 leads to 4-vinyl*cyclo*hexene.)

values with the experimental entropy of activation seemed to indicate that mechanism (*b*) is operative. It will now be shown that this mode of addition is not proved, and that a number of observations provide arguments against the supposition that in the dimerisation of butadiene or in kinetically similar diene syntheses the transient formation of free radicals takes place. It should be noted, however, that the following considerations relate to thermal Diels–Alder reactions which have been the subject of a kinetic investigation and that it is not within the scope of this paper to deal with those additions to substituted styrenes which, according to Hudson and Robinson (J., 1941, 715), are initiated by the part formation of one co-ordinated link between the associating molecules. It is also not intended to discuss diene reactions which occur as a result of photochemical or catalytic processes or which depend on the migration of hydrogen atoms.

The Entropy of Activation in the Dimerisation of Butadiene.—The bimolecular velocity coefficient of the dimerisation of gaseous butadiene can be represented (cf. Glasstone, Laidler, and Eyring, " Theory of Rate Processes," New York, 1941, p. 198) by

$$\text{velocity coefficient} = Ae^{-E/RT} = \kappa(kT/h)e^{2}e^{\Delta S^{*}/R}e^{-E/RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where E is the Arrhenius activation energy and κ the transmission coefficient. An approximate estimate of the entropy of activation, ΔS^{*}, can be made by using the standard formulæ in Table I (see Fowler and

TABLE I.

Standard Formulæ for Entropy Calculations.

Freedom.	Contribution to S/R and to S^{*}/R.
Translation (relating to g.-mol. and cm.^{3})	$1{\cdot}299 + \log_e\left\{\left(\frac{T}{100\ \text{deg.}}\right)^{3/2} M^{3/2}\right\}$
External rotation	$3{\cdot}46 + \log_e\left\{\frac{(I'I''I''')^{1/2}}{(10^{-40}\ \text{g.-cm.}^2)^{3/2}}\left(\frac{T}{100\ \text{deg.}}\right)^{3/2}\frac{1}{\sigma}\right\}$
Harmonic vibration	$\frac{\Theta/T}{e^{\Theta/T}-1} + \log_e\{(1-e^{-\Theta/T})^{-1}\}$
Internal rotation	$1{\cdot}54 + \log_e\left\{\left(\frac{i}{10^{-40}\ \text{g.-cm.}^2}\right)^{1/2}\left(\frac{T}{100\ \text{deg.}}\right)^{1/2}\frac{1}{\sigma_i}\right\}$

Guggenheim, " Statistical Thermodynamics," Cambridge, 1939), in which the symbols have the following meanings : M is the molecular weight on the conventional chemical scale, I', I'', I''' are the principal moments of inertia, σ is the external symmetry number, Θ is the frequency of a harmonic internal vibration expressed in terms of temperature by using the relation $h\nu = kT$, i is the reduced moment of inertia, and σ_i is the symmetry number appropriate to the internal rotations. In applying some of these formulæ it has to be borne in mind that butadiene and the two types of activated complex are resonance hybrids, so that in principle the entropy should be computed for a number of different contributing structures. The calculations in this communication relate, however, to one set of bond assignments only. These are as follows. *Butadiene :* the ordinary formula is employed. *Cyclic activated complex :* the two carbon–carbon bonds between the atoms 1, 6 and 4, 5 are not fully formed (cf. below) but otherwise the bond assignment is regarded as identical with that in 4-vinyl*cyclo*hexene. *Open-chain activated complex :* the species here considered is assumed to be identical with (I), except in so far as the carbon–carbon bond between atoms 4 and 5 is not fully formed. Kistiakowsky and Ransom assumed that (I) consists both of a triplet, and a singlet state of nearly equal energy, whereas butadiene is, of course, in a singlet state. The supposed change of electron multiplicity was taken care of by a term R ln 4, which was added to the other entropy contributions. This procedure has not been adopted, for it is not clear how a singlet state can change with sufficient speed, in the absence of a magnetic field, into a triplet state. It should be noted, however, that the coupling between the spins of the electrons designated by

the four dotted vertical lines in (I) will be so loose that species (I) can at any rate be described as a " diradical " even if a triplet state is not formed, and that the term $\boldsymbol{R}$ ln 4 is numerically smaller than the inaccuracies of the rotational and vibrational entropy contributions, so that it is irrelevant for all the following conclusions whether it is included in the total entropy change or whether it is omitted. The possible formation of a branched-chain isomer of (I) has been disregarded by Kistiakowsky and Ransom and, therefore, it is not necessary to estimate the entropy of this stereochemically different radical.

The lengths of the C—C, C···C, and C=C bonds in all the above species have been assumed to be respectively 1·5, 1·4, and 1·35 A. It is realised that the bond lengths of ordinary molecules and activated complexes cannot exactly agree, but the difference can be neglected for the purpose of the present approximate entropy calculations, which relate moreover to species the stereochemical configuration of which is unknown.

TABLE II.

Data for Calculation of Contributions due to Translation and External Rotation.

		Butadiene.	Activated complex. Cyclic.	Open-chain.
M		54·1	108	108
$(I'I''I''')^{1/2}\ 10^{38}$ / g.-cm.^{3}	Maximum	10	98	110
	Minimum	6	78	10
	Mean	8	88	60
σ		2	1	2

The principal moments of inertia in Table II, which are required for the estimation of the various contributions due to the external rotations, are the roots of the secular equation (3), where m is the mass of the CH

$$\begin{vmatrix} \Sigma m(y^2+z^2)-I & \Sigma mxy & \Sigma mxz \\ \Sigma myx & \Sigma m(z^2+x^2)-I & \Sigma myz \\ \Sigma mxz & \Sigma myz & \Sigma m(x^2+y^2)-I \end{vmatrix} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and CH_2 group and x, y, and z are their rectangular co-ordinates referred to the centre of gravity of the molecule and with arbitrary directions. The reactants and the activated complexes were represented by models of steel wire in which the hydrogen atoms coincided with adjacent carbon atoms (cf. Kistiakowsky and Ransom) and the bond angles were between the tetrahedral angle and 120°. The models were so large that the co-ordinates of the various CH and CH_2 groups could be estimated by carrying out measurements with a ruler, the distances so obtained being 10^9 times larger than the relevant x, y, or z values of equation (3). The maximum and minimum moments of inertia in Table II refer in the case of butadiene to the plane *cis*- and *trans*-form, and in the case of the cyclic activated complex to configurations which are distinguished by the position of the extracyclic vinyl group. The maximum moments of inertia of the open-chain activated complex relate to an extended zigzag form which is similar to the grouping of the middle part of the diphenyloctatetraene molecule in the solid state (Kuhn and Hengstenberg, *Z. Krist.*, 1930, **75**, 301), while the minimum moments of inertia refer to a closely packed configuration in which the CH and CH_2 groups are in the corners of a distorted cube.

The contributions due to harmonic vibrations and internal rotations were estimated by using Pitzer's rules (*J. Chem. Physics*, 1937, **5**, 469, 473) and the formulæ in lines 3 and 4 of Table I. The vibrational and rotational classes, the number of modes, and the assumed frequencies are listed in Table III, which for reasons given below is divided into two parts α and β. The data relate to two butadiene molecules, to the cyclic and the open-chain activated complex, and, for the sake of comparison, reference is also made to the relevant fully formed associated species. The difference between the latter molecules and the activated complexes is assumed to consist in the number of those carbon–carbon stretching and bending modes which are listed in lines 5 and 9 of Table III. It should be noted that the cyclic and the open-chain activated complex have only respectively four and two C···C stretching modes. This is due to the fact that the normal vibrational frequency in the co-ordinate of reaction has an imaginary value.

All the vibrational frequencies except the one indicated by an asterisk were taken from Kistiakowsky and Ransom, who computed the vibrational entropy of butadiene and of the open-chain activated complex by using Pitzer's method. For the cyclic species, however, they estimated the total entropy with the help of thermochemical data and of an empirical rule for the calculation of heat capacities. The present computation of the entropy of the cyclic activated complex has been carried out by using the same method as that employed for the other species and involves the assumption that the frequencies of all the carbon–carbon bending modes are equal to each other and are as low as 190 cm.$^{-1}$. Although in benzene or simple aromatic compounds such low frequencies do not occur (cf., *e.g.*, Lord, Ahlberg, and Andrews, *J. Chem. Physics*, 1937, **5**, 649), it is nevertheless believed that the above estimate is not unreasonable, for data have been presented (Wassermann, *Proc. Roy. Soc.*, 1941, *A*, **178**, 370) which are consistent with the assumption that in certain derivatives of *cyclo*hexene some of the vibrational frequencies are as low as 190 cm.$^{-1}$ or even lower. Kistiakowsky and Ransom referred to a cyclic activated complex stereochemically similar to 4-vinyl*cyclo*hexene with " a half dozen frequencies of 150 cm.$^{-1}$ " and pointed out that this assignment would bring theory and experiment together, but in contrast with the present point of view they regarded the assumption of low frequencies as so improbable that the stepwise mechanism of the formation and decomposition of 4-vinyl*cyclo*hexene was believed to be proved.

TABLE III.

Data for Calculation of Contributions due to Vibrations and Internal Rotations.

	Vibrational class (including internal rotations).	Number of vibrations or internal rotations. 2 Butadiene.	Activated complex. Cyclic.	Activated complex. Open-chain.	Fully-formed associated species. Cyclic.	Fully-formed associated species. Open-chain.	Frequency ($cm.^{-1}$).
α	1. C—H stretching	12	12	12	12	12	3000
α	2. $\begin{matrix}H\\H\end{matrix}\!\!>$C bending	4	4	4	4	4	1440
α	3. H—C—C, H—C=C, or H—C≡C bending	8	8	8	8	8	950
α	4. $\begin{matrix}H\\H\end{matrix}\!\!>$C—C, $\begin{matrix}H\\H\end{matrix}\!\!>$C=C, or $\begin{matrix}H\\H\end{matrix}\!\!>$C≡C bending	8	11	10	11	10	950
α	5. C—C stretching	2	4	2	6	3	1000
α	6. C=C stretching	4	2	—	2	—	1600
α	7. C≡C stretching	—	—	4	—	4	1335
α	8. C=C—C, C≡C—C, or C—C—C bending	4	—	4	—	4	320
α	9. C=C—C or C—C—C bending	—	10 †	—	9	—	190 *
α	10. C≡C—C bending	—	—	2	—	2	336
β	11. $\begin{matrix}H\\H\end{matrix}\!\!>$C=C torsion	4	1	—	1	—	570
β	12. $\begin{matrix}H\\H\end{matrix}\!\!>$C≡C torsion	—	—	2	—	2	—
β	13. C≡C torsion	—	—	2	—	2	—
β	14. C—C internal rotation	2	1	3	1	3	—

† The mode which does not appear in the fully-formed 4-vinyl*cyclo*hexene corresponds to a twisting of four carbon atoms and six hydrogen atoms relative to the rest of the molecule.

The normal modes indicated in lines 1—11 of Table III were treated as harmonic vibrations, but the contributions of the modes referred to in the last three lines were calculated with the help of the formula in line 4 of Table I and the data in Table IV. The reduced moments of inertia, i, relating to the rotation about the bonds

TABLE IV.

Data for Calculation of Contributions due to some of the Torsional Modes.

	Rotation about	i (10^{39} g.-cm.^{2})	σ_i.
Butadiene	C—C	$2 \pm 0{\cdot}5$	1
Cyclic activated complex	C—C (vinyl group)	27 ± 3	1

	Rotation about	i (10^{39} g.-cm.^{2})	σ_i.
Open-chain activated complex	$\overset{1}{C}\equiv\overset{2}{C}$ and $\overset{7}{C}\equiv\overset{8}{C}$	$0{\cdot}3 \pm 0{\cdot}2$	2
	$\overset{2}{C}\equiv\overset{3}{C}$ and $\overset{6}{C}\equiv\overset{7}{C}$	4 ± 2	1
	$\overset{3}{C}-\overset{4}{C}$ and $\overset{5}{C}-\overset{6}{C}$	6 ± 2	1
	$\overset{4}{C}-\overset{5}{C}$	24 ± 8	1

$\overset{1}{C}\equiv\overset{2}{C}$ and $\overset{7}{C}\equiv\overset{8}{C}$ of the open-chain activated complex were estimated on the assumption that the C—H distance is 1·1 A., but the other i values relate to molecular models in which the hydrogen atoms were treated as coinciding with adjacent carbon atoms. All the reduced moments of inertia were calculated both for extended and for closely packed configurations, the figures in cols. 3 and 7 of Table IV being the means of the relevant maximum and minimum values. The mode designated in Table III by " C—C internal rotation " was treated as free internal rotation; a correction due to a restricting potential would not alter any of the following conclusions even if it were assumed that the potential is as high as 3 kg.-cals./mol. The contributions of the modes designated by $\begin{matrix}H\\H\end{matrix}\!\!>$C≡C torsion and C≡C torsion are the means of two sets of values which were obtained by assuming that the bonds between the atoms 1, 2, 3, and 6, 7, 8 of the open-chain activated complex are (*a*) ordinary single bonds and (*b*) ordinary double bonds. In calculating set (*a*), the free rotator treatment was applied and the data in lines 1 and 2 in col. 7 of Table IV were used. Set (*b*), on the other hand, relates to harmonic torsional vibrations and to frequencies which were estimated by allowing for the same force constant as that of the torsional mode in ethylene (cf. papers referred to by Gallaway and Barker, *J. Chem. Physics*, 1942, **10**, 88). This method is somewhat different from that employed by Kistiakowsky and Ransom, who calculated the relevant contributions by applying the harmonic oscillator formula and by estimating the relevant frequency on the assumption that the force constant is one half of that of the torsional vibration of ethylene.

The quantity of $\Delta S^*/\boldsymbol{R}$ of equation (2) can be regarded as being the sum of three terms :

$$\Delta S^*/\boldsymbol{R} = [\Delta S^*_{\text{rig.}} + \Delta S^*_{\text{vib. }(\alpha)} + \Delta S^*_{\text{vib. }(\beta)}]/\boldsymbol{R} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where $\Delta S^*_{\text{rig.}}/\boldsymbol{R}$ comprises the contributions of the various species supposed to be rigid, and $\Delta S^*_{\text{vib. }(\alpha)}/\boldsymbol{R}$ and $\Delta S^*_{\text{vib. }(\beta)}/\boldsymbol{R}$ relate respectively to the stiff vibrations listed in Part α of Table III and to the looser vibrations and internal rotations mentioned in Part β. The various contributions to $[\Delta S^*_{\text{rig.}} + \Delta S^*_{\text{vib. }(\alpha)}]/\boldsymbol{R}$ are in Table V, those to $[\Delta S^*_{\text{vib. }(\beta)}]/\boldsymbol{R}$ are in Table VI, and a summary of all the numerical results of the entropy

TABLE V.

Contributions to $[\Delta S^*_{\text{rig.}} + \Delta S^*_{\text{vib. (a)}}]/R$ ($T = 600°$).

Freedom.	2 Butadiene.	Activated complex. Cyclic.	Open-chain.
Translation (relating to g.-mol. and cm.³)	20·0	11·0	11·0
External rotation	24·2 ± 0·8	15·2 ± 1	14·0 ± 1·5
Vibration (a)	7·8	9·4	9·5
Sum	52·0	35·6	34·5

TABLE VI.

Contributions to $\Delta S^*_{\text{vib. }(\beta)}/R$ ($T = 600°$).

Freedom.	2 Butadiene.	Activated complex. Cyclic.	Open-chain.
C≡C—C, C≡C—C, or C—C—C bending	5·1	20·1	5·1
C≡C≡C bending	—	—	2·5
H, H>C=C torsion	3·2	0·8	—
H, H>C=C torsion	—	—	3·1
C≡C torsion	—	—	7·6
C—C internal rotation	7·8 *	4·1	10·9
Sum	16·1	25·0	29·2

* It follows from this value and from the figure in the first line of Table V that $(S_{\text{rig.}} + S_{\text{C–C internal rotation}})/R = 52·0$ for two butadiene molecules, which agrees with Kassel's computation (*J. Chem. Physics*, 1936, **4**, 435); it should be noted that in the above tables $S_{\text{translation}}$ relates to g.-mols. and cm.³, whereas Kassel's translational entropy relates to 1 atm.

TABLE VII.

Summary of Numerical Results of Entropy Calculations ($T = 600°$).

	Activated complex. Cyclic.	Open-chain.	Comment.
$[\Delta S^*_{\text{rig.}} + \Delta S^*_{\text{vib. (a)}}]/R$	−16·4	−17·5	Present computation.
$\Delta S^*_{\text{vib.}(\beta)}/R$	+ 8·9	+13·1	Present computation.
$\Delta S^*/R$	− 7·5	− 4·4	Present computation.
$\Delta S^*/R$	−16·7	− 8·6	Kistiakowsky and Ransom.

calculations is in Table VII. It should be noted that the difference between the two values in the first line of Table VII is smaller than the inaccuracy due to the incomplete knowledge of the principal moments of inertia. The means of the two sets of $\Delta S^*/R$ values listed respectively in line 3 and 4 of Table VII are :

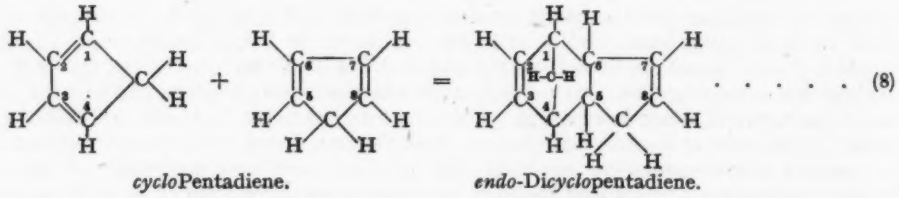
$$\Delta S^*/R = -12 \pm 5 \text{ for cyclic activated complex} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$\Delta S^*/R = -6 \pm 3 \text{ for open-chain activated complex} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

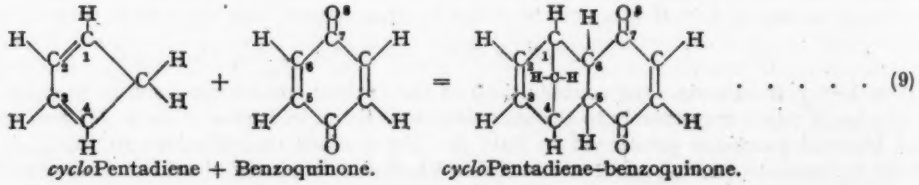
It follows from Kistiakowsky and Ransom's kinetic measurements that the non-exponential A factor of equation (2) is $10^{9·96 \pm 0·18}$ cm.³/g.-mol. sec., so that

$$\Delta S^*_{\text{exptl.}}/R = 2·30\,(9·96 - \log_{10}\kappa - \log_{10} kT/h - 2\log_{10} e) \quad . \quad . \quad . \quad . \quad . \quad (7)$$

If the transmission coefficient κ is assumed to be unity $\Delta S^*_{\text{exptl.}}/R$ would equal $-9·2 \pm 0·5$ at $T = 600°$, which is compatible with both (5) and (6). Thus the theoretical method cannot be used in order to find out whether the dimerisation of butadiene or the reverse decomposition of 4-vinyl*cyclo*hexene involves the transient formation of open-chain radicals. It is possible, however, that entropy calculation will lead to more conclusive results if new spectroscopic and thermochemical data relating to the participants of reaction (1) should become available.



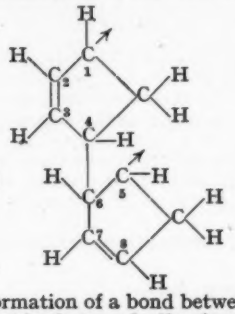
*cyclo*Pentadiene. *endo*-Di*cyclo*pentadiene. (8)



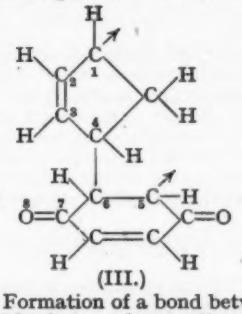
*cyclo*Pentadiene + Benzoquinone. *cyclo*Pentadiene–benzoquinone. (9)

Arguments against a Mechanism involving Free Radicals.—The dimerisation of butadiene is chemically and kinetically of the same type as the diene syntheses (8) and (9). If the mechanism of these associations is stepwise, then the structure of the rate-determining activated complexes might be as in (II) or (III).

(II.)



Radical II. Formation of a bond between the carbon atoms 1 and 5 leads to *endo*-di*cyclo*pentadiene.



(III.)

Radical III. Formation of a bond between the carbon atoms 1 and 5 leads to *cyclo*pentadiene–benzoquinone.

The associations (8) and (9) involve relatively complex molecules and, therefore, a sufficiently accurate *a priori* calculation of the entropy of activation is more difficult than in the case of reaction (1). There is, however, a qualitative method of approach in order to gain information about the nature of intermediates in all these diene syntheses which refers to an interpretation of the results of rate measurements carried out both in the presence of a relatively large amount of oxygen or peroxides and under conditions under which these latter substances were excluded from the reaction mixture as far as possible. The following observations were made in these experiments.

Reactions of butadiene which occur wholly in the gas phase. Vaughan (*J. Amer. Chem. Soc.*, 1932, **54**, 3863) treated butadiene with hexaphenylethane in order to remove the last traces of oxygen or peroxides, but this had no measurable influence on the rate of the low-molecular polymerisation, the course of this process being followed by measuring the pressure change at constant volume. In one experiment at 646° K. a relatively large amount of oxygen was added to the reaction mixture, with the result that the rate of pressure change increased by about 30%. The present author believes that this oxygen effect does not relate to the dimerisation of butadiene but to consecutive reactions of higher activation energy.* If this assumption is correct, it would be expected that at a lower temperature the oxygen influence is less pronounced because under the latter conditions the observed pressure change is more closely related to the dimerisation reaction. Kistiakowsky and Ransom (*loc. cit.*, Table II) found, in fact, that at a temperature which was 119° lower than that obtaining in Vaughan's experiment catalysis by molecular oxygen could not be detected.

Homogeneous reactions of liquid butadiene. Koblianski and Piotrovski (*Synt. Kauchouk*, 1936, **5**, No. 3, 3) did a series of measurements from which it follows that the macropolymerisation of butadiene is accelerated by oxygen,† while the rate of the dimerisation process is not detectably altered. It appears, therefore, that the primary steps in the macro-polymerisation and in the dimerisation of butadiene are fundamentally different, and that the formation of 4-vinyl*cyclo*hexene should not be regarded as a side reaction of the low-molecular link of a polymerisation chain.‡

Dimerisation of cyclo*pentadiene and addition of* cyclo*pentadiene to benzoquinone.* Stobbe and Reuss (*Annalen*, 1912, **391**, 151), Schultze (*J. Amer. Chem. Soc.*, 1934, **56**, 1552), Harkness, Kistiakowsky, and Mears (*J. Chem. Physics*, 1937, **5**, 682), Benford, Kaufmann, Khambata, and Wassermann (J., 1939, 362, 375, 381), and Raistrick, Sapiro, and Newitt (*ibid.*, p. 1764) found that the rate of these associations is not influenced by oxygen or by peroxides, the various experiments being carried out between 287 and 450° K. and between 1 and 4,000 atm.

Species such as (I), (II), or (III) should combine quickly with molecular or peroxide oxygen, these reactions being probably faster than the oxidation of the alternative type of activated complexes. If, therefore, the transient formation of diradicals played a rôle, oxygen or peroxide should produce a marked change of the course of the overall associations. Since an effect of this kind has not been observed, it seems on the whole more justifiable to assume that the rate-determining step of bimolecular diene syntheses involves activated complexes which are stereochemically similar to the fully formed products.

The author is grateful to Dr. E. A. Guggenheim for many valuable discussions.

IMPERIAL COLLEGE AND UNIVERSITY COLLEGE, LONDON. [*Received, August 6th*, 1942.]

* Kistiakowsky and Ransom refer to one of the possible consecutive reactions, *viz.*, the addition of butadiene to 4-vinyl-Δ^3-*cyclo*hexene to produce $\Delta^3:3'$-octahydrodiphenyl. The activation energy of this process is assumed to be 38 kg.-cals., whereas that of the dimerisation of butadiene amounts to 23·7 kg.-cals. $\Delta^3:3'$-Octahydrodiphenyl was isolated in the liquid state, in the presence of acetylenedicarboxylic acid in a yield of 5% of the theoretical amount (Alder and Rickert, *Ber.*, 1938, **71**, 373). There is no evidence that under the conditions of the experiments of Kistiakowsky and Ransom the consecutive reactions referred to above include the 1 : 4–1 : 2 addition of butadiene and 4-vinyl*cyclo*hexene.

† It is possible that the oxygen effect is related to the irreversible formation of oxidised polybutadienes; cf. Chochlovkin, *Synt. Kauchouk*, 1936, **5**, No. 4, 12.

‡ This conclusion is in agreement with observations made by Saveliev, Arbirdan, and Zlatogurski (*Synt. Kauchouk*, 1936, **5**, No. 4, 18), who found that copper naphthenate and copper oleate are inhibitors in the macro-polymerisation of butadiene, but that they do not affect the rate of the dimerisation reaction.

127. *Homogeneous Catalysis of Diene Syntheses. A New Type of Third-order Reaction.*

By Albert Wassermann.

The rate of diene syntheses (Diels–Alder reactions) is not detectably altered on addition of iodoacetic acid, *p*-toluenesulphonic acid, pyridine, 2 : 2′-dipyridyl, three salts of heavy metals, iodine, *trans*-stilbene, oxygen, peroxides, acetonitrile, or ethyl trichloroacetate. Trichloroacetic acid, on the other hand, as well as a number of other acids, one base (*viz.*, trimethylamine), and α-naphthaquinone, are catalytically active. The latter tests were made in both polar and non-polar solvents, and in one association a rate-accelerating effect of an acid could also be detected in the gas phase, there being no doubt that all the catalytic processes are homogeneous. An investigation of the kinetics of a selected set of catalytic processes showed that the primary step is of the third order and that the activation energy is near to zero.

Experiments are described relating to the catalysis of the following associations which are all typical diene syntheses :

*cyclo*Pentadiene + Benzoquinone = *cyclo*Pentadiene–benzoquinone . . . . . (I)
*cyclo*Pentadiene + α-Naphthaquinone = *cyclo*Pentadiene–α-naphthaquinone . . . . . (II)
2 *cyclo*Pentadiene = *endo*-Di*cyclo*pentadiene . . . . . (III)
*cyclo*Pentadiene + *cyclo*Pentadiene–benzoquinone = Di*cyclo*pentadiene–benzoquinone . . . . . (IV)
*cyclo*Pentadiene + Tetrachlorobenzoquinone = *cyclo*Pentadiene–tetrachlorobenzoquinone . . . . . (V)

Catalytic tests involving 36 added substances were made; the results of the various sets of measurements, numbered for further reference, are in Table I.

Table I.

Influence of various added substances on the rate of diene syntheses.

Ref. No.	1.	2.	3.	4.	5.
Substance tested	H_2SO_4	H_3PO_4	HCl	12 Organic bases	$CH_2I{\cdot}CO_2H$
Solvent	Paraffin	Paraffin	EtOH	EtOH and C_6H_6	C_6H_6
Diene synthesis	III	III	I	I	I
Catalytic efficiency	?	?	?	?	—
Ref. No.	6.	7.	8.	9.	10.
Substance tested	*p*-$C_6H_4Me{\cdot}SO_2H$	C_5H_5N	2 : 2′-Dipyridyl	$FeCl_3$	$CuCl_2$
Solvent	EtOH	C_6H_6	C_6H_6	EtOH	EtOH
Diene synthesis	I	I	I	I	I
Catalytic efficiency	—	—	—	—	—
Ref. No.	11.	12.	13.	14.	15.
Substance tested	$MnCl_2$	I_2	*trans*Stilbene	O_2	Di*cyclo*pentadiene peroxide
Measurements done in	EtOH	C_6H_6	EtOH	C_6H_6, CCl_4, gas	$C_{10}H_{12}$
Diene synthesis	I	I	I	I and III	III
Catalytic efficiency	—	—	—	—	—
Ref. No.	16.	17.	18.	19.	20.
Substance tested	Bz_2O_2	MeCN	$CCl_3{\cdot}CO_2Et$	PhOH	$CH_2Br{\cdot}CO_2H$
Solvent	C_6H_6	CCl_4	C_6H_{14}	C_6H_6	C_6H_6
Diene synthesis	III	III	I	I	I
Catalytic efficiency	—	—	—	+	+
Ref. No.	21.	22.	23.	24.	25.
Substance tested	$CH_2Cl{\cdot}CO_2H$		$CCl_3{\cdot}CO_2H$		NMe_3
Solvent	C_6H_6	EtOH	C_6H_{14}	C_6H_6	C_6H_6
Diene synthesis	I	I	I	I	I
Catalytic efficiency	+	+	+	+	+
Ref. No.	26.	27.	28.	29.	30.
Substance tested	$CCl_3{\cdot}CO_2H$	α-Naphthaquinone	$CCl_3{\cdot}CO_2H$	NMe_3	$CH_3{\cdot}CO_2H$
Measurements done in	C_6H_6	C_6H_6	C_6H_6 and Paraffin	C_6H_6	Gas
Diene synthesis	II	I	III, IV, V	V	III
Catalytic efficiency	+	+	+	+	+

The experiments with sulphuric, phosphoric and hydrochloric acids and certain organic bases did not lead to conclusive results. Iodoacetic acid,* *p*-toluenesulphonic acid,* pyridine,* 2 : 2′-dipyridyl,* three salts of heavy metals,* iodine,* *trans*-stilbene,* oxygen,* peroxides,* acetonitrile,* and ethyl trichloroacetate are ineffective, but phenol, bromoacetic acid,† chloroacetic acid, trichloroacetic acid, trimethylamine, α-naphthaquinone, and acetic acid are catalytically active. These experiments were carried out in polar and non-polar solvents and in one case a rate-accelerating effect was found to occur in the gas phase, all the catalysed diene syntheses being entirely homogeneous.

* The experiments involving the substances indicated by an asterisk have already been described in previous papers; for references, see this vol., p. 623 (cf. also J., 1935, 828).

† This acid was described as being inactive (see J., 1935, 828); more accurate measurements showed, however, that there is a weak catalytic effect.

In attempting to elucidate the kinetics of the catalysed reactions Nos. 19—26, velocity coefficients, v_c, were calculated from

$$dx/dt = v_c(a - x)^2 c + v(a - x)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where a and $a - x$ are the equimolar concentrations of the reactants at zero time and time t, respectively, c is the stoicheiometric concentration of the rate-accelerating added substance, and v is the bimolecular velocity coefficient of the non-catalysed diene syntheses taken from earlier papers of this series (J., 1935, 828; 1936, 1028). The various v_c values are in Table II, which also refers to the temperature and concentration range in which (1) was tested and to the number of runs in each set of measurements.

TABLE II.

Catalytic velocity coefficients, v_c, *relating to the formation of* cyclo*pentadiene–benzoquinone and* cyclo*pentadiene–α-naphthaquinone.*

Ref. No.	Diene synthesis.	Catalyst.	Solvent.	Temp.	$\log_{10} v_c$.*	Concentration range (g.-mols./l.). Catalyst.	Reactant at $t = 0$.	No. of runs.
19		PhOH		25°	−0·9 ± 0·1	0·0012—0·2	0·02	6
20		$CH_2Br{\cdot}CO_2H$	C_6H_6	25	−0·70 ± 0·06	0·01—0·04	0·02	2
21		$CH_2Cl{\cdot}CO_2H$		25	−0·70 ± 0·06	0·0025—0·04	0·02	3
22			EtOH	21	−0·22 ± 0·07	0·01	0·005	1
23			C_6H_{14}	25	+0·58 ± 0·04	0·0025—0·01	0·02	4
	I			12·5	+0·52 ± 0·04	0·005	0·02	1
				20	+0·51 ± 0·04	0·005	0·02	1
24		$CCl_3{\cdot}CO_2H$		25	+0·48 ± 0·04	0·0025—0·01	0·005—0·03	10
			C_6H_6	39	+0·52 ± 0·04	0·005	0·02	1
				53	+0·36 ± 0·12	0·005	0·02	1
25		NMe_3		12	−0·1 ± 0·1	0·005—0·01	0·02	2
26	II	$CCl_3{\cdot}CO_2H$		25	+0·04 ± 0·04	0·0025—0·01	0·02	5

* v_c is given in the units l.^{2} g.-mol.$^{-2}$ sec.$^{-1}$ both here and in Tables III and IV.

In Expts. Nos. 19—22 equation (1) was found to hold, the relevant catalytic velocity coefficients being the arithmetic means of the consistent v_c values as observed at various times and with different catalyst concentrations. In Expts. Nos. 23—26, on the other hand, the v_c values as deduced from (1) decrease with increasing time, probably owing to consecutive and reverse processes taking place * and to the formation of a relatively inactive complex between catalyst and product. The occurrence of the latter effect is indicated by experiments showing that *cyclo*pentadiene–benzoquinone acts as an inhibitor in the trichloroacetic acid catalysis of diene synthesis (I). The catalytic velocity coefficients Nos. 23—26 in Table II were estimated by plotting the relevant observed v_c values against time and extrapolating the graph so obtained to zero conversion. In all cases the initial v_c values were independent of the catalyst concentration, and in those runs in which tests were made there was also no detectable influence of the initial concentration of the reactants.

Atomic recombinations or acid- and base-catalysed reactions which have been the subject of previous kinetic investigations (cf. Bell, " Acid–Base Catalysis," Oxford, 1941, p. 114) do not take place at all in the absence of the catalyst, whereas the diene syntheses here considered proceed with measurable speed even in aprotic solvents or wholly in the gas phase, the non-catalysed associations being bimolecular. In the presence of the substances listed in col. 3 of Table II, a third-order catalysed reaction proceeds simultaneously with the bimolecular diene syntheses. This follows from the results of the kinetic measurements, which show that at least during the initial stage equation (1) is obeyed. A kinetic investigation of the catalytic processes Nos. 27—30 in Table I has not yet been carried out; it is believed, however, that the primary step is similar to that obtaining in Nos. 22—26.

It should be noted that the initial v_c value relating to the trichloroacetic acid catalysis of reaction (I) in benzene solution is not measurably affected by a temperature change within a range of about 40°; it follows, therefore, that the activation energy is numerically smaller than 1·5 kg.-cals.† This is an independent confirmation of the assumption that the reaction is of the third order, for it is known that some authentic third-order processes (*e.g.*, the reaction of nitrogen oxide with oxygen) are also characterised by relatively small activation energies.

It is intended to continue this research with a view to find out whether the homogeneous catalysis of diene syntheses is dependent on proton-transfer processes or whether an essentially different mechanism is operative.

EXPERIMENTAL.

The participants of reactions (I)—(IV) and the various solvents were purified by methods indicated in preceding parts of this series; the paraffin was the same specimen as that mentioned in J., 1939, 369; tetrachlorobenzoquinone and the product of reaction (V) were recrystallised respectively from benzene and ethyl alcohol, and all the substances which were tested for catalytic activity were recrystallised or redistilled and carefully dried. In the experiments with acids in ethyl-alcoholic solutions, titration tests showed that no detectable esterification had taken place. The stoi-

* In the case of diene synthesis (I), for instance, the consecutive process consists in the formation of di*cyclo*pentadiene–benzoquinone; the detectable influence of the reverse reaction is due to the fact that some of the runs were done at relatively high temperature.

† The overall activation energy relating to both the non-catalysed and the catalysed association amounts to about 3 kg.-cals. (cf. this vol., p. 624).

cheiometric equation of the catalysed addition of *cyclo*pentadiene to α-naphthaquinone, *cyclo*pentadiene–benzoquinone, and tetrachlorobenzoquinone was established by evaporating the solvent at the end of the reaction and weighing the purified residues, which were found to be identical with the products of the non-catalysed diene syntheses (II), (IV), and (V) and were obtained in a yield of at least 90% of the theoretical. In determining the stoicheiometric equation of the catalysed addition of *cyclo*pentadiene to benzoquinone, the product was first converted into di*cyclo*pentadiene–benzoquinone, the yield of which was then estimated as described above. This procedure had to be adopted because control experiments showed that in the presence of some of the catalysts *cyclo*pentadiene–benzoquinone is either decomposed during the evaporation of the solvent or undergoes subsequent changes leading to products which could not be identified. A typical experiment is as follows. 450 C.c. of a benzene solution, which at zero time was 0·09M with respect to *cyclo*pentadiene and benzoquinone and 0·05M with respect to trichloroacetic acid, are kept at 25° until 95% of the benzoquinone has reacted. Evaporation of the solvent at room temperature would now afford a non-crystallisable syrup, but if, instead, 6 c.c. of pure liquid *cyclo*pentadiene are added to the solution which is then kept at 50° for 54 hours, di*cyclo*pentadiene–benzoquinone can be isolated in a yield of 92% of the theoretical.

In order to establish that all the catalytic reactions referred to in this paper are homogeneous, control experiments with added glass powder or glass rods were carried out.

Reactions (I), (II), and (IV).—Velocity measurements were carried out by the methods already described (*locc. cit.*), all colorimetric determinations referring as before to filter S_{47} of the Zeiss Stufenphotometer. Hydrochloric acid in ethyl alcohol reacts with benzoquinone (cf. Gattermann–Wieland, "Die Praxis des Organischen Chemikers," Berlin, 1925, p. 281), thereby causing fading of its colour, the rate of fading being influenced by traces of impurities. It was not possible, therefore, to find out whether hydrochloric acid in ethyl alcohol is a catalyst for reaction (I) or not.

Attempts were made to follow the course of reaction (I) in the presence of methylamine, ethylenediamine, aniline, piperidine, 7-methylindole, pyrrole, cystein hydrochloride, glycylglycine, *l*-aspartic acid, *l*-leucine, *l*-tyrosine, and tryptophan. Deep colorations are produced on addition of a solution of benzoquinone in benzene or ethyl alcohol to any of the first seven bases; the other bases are also unsuitable for tests in ethyl alcohol or benzene, for their solubility is too small.

Control experiments showed that the extinction coefficient of benzoquinone is not measurably altered on addition of the substances listed in Nos. 18—25 and No. 27 of Table I, and that the colour of α-naphthaquinone is not detectably altered on addition of trichloroacetic acid.

TABLE III.

Catalysis of diene syntheses (I) and (II)—typical experiments.

Temp.: (22), (27) = 20°; (19), (20), (21), (23), (26) = 25°; (24), (25) = 12·5°.
Concn. of catalyst (g.-mols./l.): (19) = 0·200; (20), (22), (26) = 0·0100; (21) = 0·00250; (23), (24), (25) = 0·00500; (27) = 0·00100.
Initial concn. of reactants (g.-mols./l.): (22) = 0·00500; (19), (20), (21), (23), (24), (25), (26) = 0·0200; (27) = 0·001 ($C_6H_4O_2$) and 0·002 (C_5H_6).

Ref. No. (19).			Ref. No. (20).			Ref. No. (21).			Ref. No. (22).			Ref. No. (23).		
Time, mins.	η, cm.$^{-1}$.*	v_c.	Time, mins.	η, cm.$^{-1}$.*	v_c.	Time, mins.	η, cm.$^{-1}$.*	v_c.	Time, mins.	η, cm.$^{-1}$.*	v_c.	Time, mins.	η, cm.$^{-1}$.*	v_c.
10	0·246	6·8	20	0·268	12	20	0·278	12	5	0·0645	40	10	0·210	240
15	0·222	6·2	30	0·233	11	30	0·252	12	15	0·0585	30	20	0·176	220
22	0·154	5·8	40	0·223	11	40	0·232	12	30	0·0516	30	30	0·153	220
35	0·150	6·3	50	0·205	10	50	0·214	16	45	0·0456	40	40	0·138	200
59	0·104	5·4	60	0·188	12	60	0·200	12	—	—	—	50	0·127	188
												60	0·115	188

Ref. No. (24).			Ref. No. (25).			Ref. No. (26).			Ref. No. (27).		
15·5	0·245	206	16	0·297	46	35	0·131	57	400	0·0205	280
28·5	0·205	186	36	0·262	40	45	0·122	53	1556	0·0136	270
39·5	0·185	168	68	0·234	22	65	0·105	49			
63	0·149	158	109	0·198	22	108	0·0846	46			
101	0·122	132	234	0·150	10	168	0·0641	40			
162	0·0911	125									

* η = Extinction coefficient.

The effects of the various catalysts recorded in Nos. 19—27 of Tables I and II are shown by the data in Table III. Expt. No. 18 in Table I was done at 25°, the equimoarl initial concentration of the reactants being 0·02 g.-mol./l. The initial catalytic velocity coefficients relating to Nos. 23, 24, and 26 are listed in Table IV.

TABLE IV.

Initial catalytic velocity coefficients of trichloroacetic acid relating to the formation of cyclo*pentadiene–benzoquinone and* cyclo*pentadiene–α-naphthaquinone.*

Temp.	Concn., g.-mols./l. × 10^4. Reactants at t = 0.		v_c.	Temp.	Concn., g.-mols./l. × 10^4. Reactants at t = 0.		v_c.	Temp.	Concn., g.-mols./l. × 10^4. Reactants at t = 0.		v_c.
		$CCl_3{\cdot}CO_2H$.				$CCl_3{\cdot}CO_2H$.				$CCl_3{\cdot}CO_2H$.	
	Ref. No. (23).				Ref. No. (24).				Ref. No. (24), contd.		
25·0°	200	25	3·8	25·0°	200	25	2·7	25·0°	200	50	1·9 *
,,	200	50	4·0	,,	200	50	3·0	12·5	200	50	3·1
,,	200	100	3·7	,,	200	100	2·8	20·0	50	100	3·3
	Ref. No. (26).			,,	50	100	3·0	39·0	200	50	3·4
25·0°	200	25	1·0	,,	100	100	3·0	53·0	200	50	2·5
,,	200	50	1·1	,,	300	100	2·8				
,,	200	100	1·1								

* This velocity coefficient relates to a run in which the reaction mixture was at zero time 0·0117M with respect to *cyclo*pentadiene–benzoquinone. The decrease of the v_c values with increasing time is similar to that obtaining in experiment No. 24 of Table III.

The trichloroacetic acid catalysis of synthesis (IV) was investigated at 25° and in a solution 0·0433M with respect to the catalyst, the equimolar initial concentration of the reactants being 0·223 g.-mol./l. After 1300 mins., 79% of the *cyclo*pentadiene had been used; without catalyst, 30% of reaction had taken place under the same experimental conditions.

Reaction (*III*).—A mixture of *cyclo*pentadiene and trichloroacetic acid was dissolved in benzene or paraffin and kept for several days at temperatures between 0° and 25°; the reaction product was found to be not only di*cyclo*pentadiene but also a polymer or a mixture of polymers. Experiments with a view to study both the rate of the association and of the simultaneous or consecutive processes have not been done, since it is easier to investigate the trichloroacetic acid catalysis of the decomposition of di*cyclo*pentadiene. The equilibrium constant of reaction (III) cannot be substantially altered by addition of a relatively small amount of catalyst, and it follows that a substance catalysing the decomposition of di*cyclo*pentadiene will also catalyse the reverse association process. In studying the decomposition reaction in paraffin solution, the "second method" described in J., 1939, 379 was used. A number of control runs showed that diffusion processes are not rate-determining, and that trichloroacetic acid in paraffin solution does not give rise to evolution of a measurable amount of gas. The reaction vessel of 200 c.c. capacity contained in each run 25 c.c. of the solution, which was usually stirred at a speed of 750 r.p.m.; the burette in which the volumetric *cyclo*pentadiene determinations were carried out was kept at 52°. In a typical experiment the initial concentration of di*cyclo*pentadiene was 2·00 g.-mols./l., that of trichloroacetic acid was 0·0145 g.-mol./l., the pressure was 764 mm. of mercury, and the temperature of the reaction mixture was 135°. The volume of the gaseous *cyclo*pentadiene as obtained under these conditions is given in line 2 of Table V, and the data in line 3 refer to a control experiment without trichloroacetic acid. Similar experiments were carried out at 125°, 145°, and 155°, the concentration of the trichloroacetic acid being varied at each temperature from 0·008 to 0·03 g.-mol./l.

TABLE V.

*Catalysis of the decomposition of di*cyclo*pentadiene by trichloroacetic acid—typical experiment.*

Time, mins	4	8	12	16	20	25	30
Gaseous *cyclo*pentadiene, c.c. { With catalyst	3·5	6·2	7·8	9·0	10·0	10·4	11·4
Gaseous *cyclo*pentadiene, c.c. { Without catalyst	1·5	2·5	3·2	3·5	3·8	4·4	4·5

A number of experiments were done on the decomposition of di*cyclo*pentadiene in paraffin solution in the presence of syrupy phosphoric acid or aqueous sulphuric acid (50 vol. %); it was found, however, that di*cyclo*pentadiene polymerises without evolution of gaseous *cyclo*pentadiene.

The catalysis by gaseous acetic acid was studied at 110° in the apparatus described by Benford and Wassermann (J., 1939, 362). In a typical experiment the acetic acid pressure was 168·0 mm. of mercury and the initial pressure of *cyclo*pentadiene was 334·5 mm. After 350 mins. the pressure decrease was 22·0 ± 1 mm. both in the empty and in the packed reaction vessels; in a control experiment without acetic acid vapour the pressure decrease was 14 ± 1 mm. The products of several catalytic experiments were collected and jointly redistilled; there was no indication that polymeric *cyclo*pentadiene was formed.

Reaction (*V*).—Rate measurements were carried out by shaking 50 c.c. of the reaction mixture containing 3 g. of finely powdered tetrachlorobenzoquinone in a dark thermostat; after known time intervals, the solvent was evaporated at room temperature and under reduced pressure, and the purified product weighed. The results of typical experiments at 25° are in Table VI. The catalytic effect of trichloroacetic acid obtains also at 21°, 29°, and 36° and in solutions which were 0·34—1·3M with respect to *cyclo*pentadiene and 0·002—0·05M with respect to the acid; in all these runs the tetrachlorobenzoquinone was not completely dissolved at zero time.

TABLE VI.

Catalysis of the formation of cyclo*pentadiene–tetrachlorobenzoquinone—typical experiments.*

Catalyst.	Concn., g.-mols./l. C_5H_8 initially.	Concn., g.-mols./l. Catalyst.	Time of reaction, mins.	Reaction, %. Without catalyst.	Reaction, %. With catalyst.
$CCl_3{\cdot}CO_2H$	0·65	0·0100	1400	20	72
NMe_3	0·65	0·0100	1400	20	58

A rate-accelerating influence of trimethylamine with simultaneous illumination by sunlight has been described by Albrecht (*Annalen*, 1906, **348**, 45), who omitted, however, to carry out control experiments in the dark. He did not establish, therefore, whether a thermal or a photochemical catalysis of reaction (V) takes place.

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128. *Solvent Effects in Association Equilibria.*

By ALBERT WASSERMANN.

This paper deals with the thermal equilibrium between the free radical β-benzoyl-αα-diphenylhydrazyl and its dimeride dibenzoyltetraphenyltetrazan. The equilibrium constant, K, has been measured by Goldschmidt and Bader in four solvents in all of which it can be represented by $K = Be^{-\Delta H/RT}$, where B is a measure of the statistical weight of the dimeride and ΔH is the heat of reaction. It is now shown that the solvent effects consist in changes of both parameters $\log B$ and ΔH, the numerical results of the measurements suggesting a linear functional relationship between these two quantities. This is explained with the aid of correlations between the equilibrium constants and the solubilities and between entropies and heats of solution.

THE experiments here discussed deal with solvent effects in the following thermal dimerisation of a free radical:

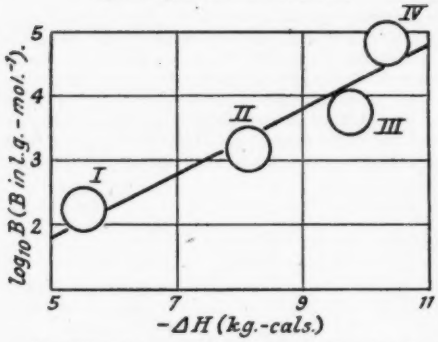
$$2NPh_2{\cdot}NBz{\cdot} = NPh_2{\cdot}NBz{\cdot}NBz{\cdot}NPh_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The equilibrium constants, K, of this reaction were measured by Goldschmidt and Bader (*Annalen*, 1929, **473**, 137) and can be represented by

$$K = [c]/[a]^2 = Be^{-\Delta H/RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where [*a*] and [*c*] are volume concentrations relating respectively to the free radical and to its dimeride, B is a measure of the statistical weight of the dimeride, and ΔH is the heat change. So far as the author is aware, these results proved for the first time that solvent effects in an association equilibrium involving electroneutral participants can be sufficiently large to produce changes in ΔH which are considerably larger than the corresponding changes in log K.* It is now shown that this experimental fact is consistent with the assumption that there is a functional linear relationship between log B and ΔH which can be explained with the help of correlations between the equilibrium constant and solubilities (van't Hoff, " Lectures on Theoretical and Physical Chemistry," 1898, Vol. 1, p. 221; Dimroth, *Annalen*, 1910, **377**, 134) and between entropies and heats of solutions (Evans and Polanyi, *Trans. Faraday Soc.*, 1936, **32**, 1335; 1937, **33**, 166; cf. also Bell, *ibid.*, 1937, **33**, 496; Butler, *ibid.*, p. 229; Barclay and Butler, *ibid.*, 1938, **34**, 1445).

Functional relationship between the parameters of the equilibrium constant.



I, *Chloroform*; II, *acetone*; III, *ether*; IV, *toluene*.

The heat changes have been computed by using

$$-\Delta H = \boldsymbol{R}T^2(\partial \ln K/\partial T)_p - \boldsymbol{R}T^2\varepsilon \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where ε is the coefficient of thermal expansion of the solvent, the B factors being obtained by substituting in (2) the ΔH values and the most reliable equilibrium constants. Experiments were carried out between $-50°$ and $-18°$, and within this range it can be assumed that both B and ΔH are not measurably altered by the temperature change. Numerical values of log K and of the two parameters of equation (2) are in the accompanying table. The suggested relationship between the figures in the last two columns is graphically represented in the figure, the magnitude of the experimental errors being indicated by the diameter of the various circles; it should be noted that the slope of the graph is about 10^{-4} cals.$^{-1}$.

Equilibrium constants, heat changes, and non-exponential B *factors relating to the thermal association of* β*-benzoyl-*αα*-diphenylhydrazyl.* (Both K and B are expressed in terms of l./g.-mol.)

Solvent.	$\log_{10} K$ at $-18°$.	$-\Delta H$ (kg.-cals.).	$-\log_{10} B$.	Solvent.	$\log_{10} K$ at $-18°$.	$-\Delta H$ (kg.-cals.).	$-\log_{10} B$.
$CHCl_3$	2·627	5·6 ± 0·6	2·2 ± 0·4	OEt_2	4·561	9·8 ± 0·7	3·8 ± 0·5
$COMe_2$	3·830	8·2 ± 0·6	3·2 ± 0·4	PhMe	3·943	10·4 ± 0·6	4·9 ± 0·4

In attempting to give a theoretical explanation for a relationship between the parameters of (2), the equation connecting the equilibrium constant, K, with the solubilities, σ, of the participants of the equilibrium is written in the form (cf. van't Hoff, Dimroth, *locc. cit.*):

$$K^m/K^n = (\sigma_a^m)^2\sigma_c^n/\sigma_c^m(\sigma_a^n)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Here and below, the superscripts indicate that the relevant quantity refers to solvents m and n, and the subscripts relate respectively to β-benzoyl-αα-diphenylhydrazyl and its dimeride. The solubilities can be represented by

$$\sigma_a = e^{\Delta S_a/R} e^{-\lambda_a/RT} = C_a e^{-\lambda_a/RT} \text{ and } \sigma_c = e^{\Delta S_c/R} e^{-\lambda_c/RT} = C_c e^{-\lambda_c/RT} \quad . \quad . \quad . \quad . \quad (5)$$

where ΔS and λ are respectively the entropies and heats of solution. If the equilibrium constants and the solubilities in (4) are substituted by products of non-exponential and exponential factors, an equation of the following form can be deduced

$$\alpha + \beta/\boldsymbol{R}T = \gamma + \delta/\boldsymbol{R}T \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where α, β, γ, and δ respectively are abbreviations for $\log B^m - \log B^n$, $\Delta H^m - \Delta H^n$, $\log C_a^n + 2\log C_a^m - \log C_c^m - 2\log C_a^n$, and $\lambda_c^n + 2\lambda_a^m - \lambda_c^m - 2\lambda_a^n$. The parameters B, ΔH, C, and λ are assumed to be not measurably affected by small temperature changes and, therefore, (6) can only be valid at different temperatures if

$$\log B^m - \log B^n = \log C_a^n + 2\log C_a^m - \log C_c^m - 2\log C_a^n \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$\Delta H^m - \Delta H^n = \lambda_c^n + 2\lambda_a^m - \lambda_c^m - 2\lambda_a^n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

The empirical correlation between entropies and heats of solution, to which reference has been made above, can be written as follows:

$$\log C_a^m - \log C_a^n = r(\lambda_a^m - \lambda_a^n) + q_a \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

$$\log C_c^m - \log C_c^n = r(\lambda_c^m - \lambda_c^n) + q_c \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Evans and Polanyi (*loc. cit.*) found that such equations, with $r \sim 10^{-4}$ cals., hold true in the case of many solute and solvent molecules of widely different chemical constitution, and it is assumed, therefore, that (9) and (10)

* It is of interest that (1) is not the only dimerisation equilibrium which has been studied in different solvents. Ziegler and Ewald (*Annalen*, 1929, **473**, 163) measured the temperature dependence of the K values relating to the association of triphenylmethyl in nine solvents, and found that the variations of ΔH and B are smaller than the experimental errors.

will also apply to the participants of the chemical equilibria the constants of which appear in equation (4). It follows that the terms on the right-hand side of (9) and (10) can be substituted for those on the right-hand side of (7). This leads to

$$\log B^{m} - \log B^{a} = r(2\lambda_{*}^{m} - 2\lambda_{*}^{a}) - r(\lambda_{\nu}^{m} - \lambda_{\nu}^{a}) + (2q_{*} - q_{\nu}) \quad . \quad . \quad . \quad . \quad . \quad (11)$$

When (8) is taken into account it follows that

$$\log B^{m} - \log B^{a} = r(\Delta H^{a} - \Delta H^{m}) + (2q_{*} - q_{\nu}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

which is the suggested functional relationship between the logarithm of the non-exponential B factor and the heat of association of the hydrazyl.

Further experiments will perhaps show that also in some other reactions $\log B$ increases linearly with ΔH, but it is not believed that the various assumptions leading to an equation of the type of (12) can always be valid. It is possible, therefore, that certain equilibria will be discovered in which a marked solvent effect obtains but in which a simple functional relationship between $\log B$ and ΔH is not apparent. Deviations from (12) are likely to occur in ionic equilibria, for in those reactions it is less justifiable to assume that the heat and entropy changes are independent of temperature than it is in associations involving electroneutral species.

IMPERIAL COLLEGE AND UNIVERSITY COLLEGE, LONDON. [*Received, August 6th,* 1942.]

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129. *Homogeneous Catalysis and Solvent Effects in a Diene Synthesis.*

By ALBERT WASSERMANN.

The catalytic and solvent effects in a diene synthesis consist in changes of both parameters of the velocity coefficient $Ae^{-E/RT}$, the observed figures suggesting a linear functional relationship between $\log A$ and E. This is explained by using a fundamental equation of the theory of absolute reaction rates in conjunction with a method similar to that described in the preceding paper.

THE experiments to be discussed deal with the diene synthesis

*cyclo*Pentadiene + Benzoquinone = *cyclo*Pentadiene–benzoquinone . . . . (1)

the rate of which has been investigated in the presence of trichloroacetic acid, which acts as a homogeneous catalyst (preceding paper) and in different polar and non-polar solvents (Wassermann, *Ber.*, 1933, **66**, 1932; J., 1935, 828; 1936, 1028; *Trans. Faraday Soc.*, 1938, **34**, 128; Fairclough and Hinshelwood, J., 1938, 236; Benford, Kaufmann, Khambata, and Wassermann, J., 1939, 381). The course of the association can be characterised by second-order velocity coefficients, v, which are represented by the Arrhenius equation

$$v = Ae^{-E/RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and it has been found that the catalytic and solvent effects consist in changes of both the non-exponential A factor and the activation energy E.*

In many chemical processes a simple correlation between these two parameters is admittedly not apparent. Fairclough and Hinshelwood (J., 1937, 538; cf. also J., 1938, 236; Hinshelwood, *Trans. Faraday Soc.*, 1938, **34**, 110, 122, 144) showed on the other hand that in the formation of quaternary ammonium salts, in diene synthesis (1), and in certain other reactions the logarithm of the non-exponential A factor increases linearly with the activation energy and they explained the suggested relationship as follows. It is supposed that two colliding particles require on the average a time t after meeting in which to reach the right internal phase for the formation of the product. If a change of chemical conditions produces an increase of certain internal vibrational frequencies of the colliding particles, the time t could be diminished and this would increase the logarithm of the non-exponential A factor. An increase of appropriate vibrational frequencies of the reactants could be connected, on the other hand, with an increase of the force constants of certain bonds which, in turn, could be associated with an increase of the activation energy. In this paper it is shown that the correlation between A and E can be explained not only with the aid of Fairclough and Hinshelwood's theory but also with the aid of a different method, in which the A factor is related to entropy changes rather than to collision frequencies. It is not within the scope of this communication, however, to discuss all those well-established reactions in which the free energy of activation is much less affected by a change of chemical conditions than the energy of activation. The following discussion relates to one example only, *viz.*, to reaction (1), but the results are expressed in a form which makes it easily possible to apply similar considerations not only to associations of the type a + b = (ab), but also to reactions of different stoicheiometric type.

Results and Discussion.—The influence of trichloroacetic acid and that of the various solvents on the kinetics of the formation of *cyclo*pentadiene–benzoquinone is shown by the data of Table I, which also contains the number of runs in each set of kinetic measurements; these were carried out between 2° and 50°, and within this range the temperature-dependence of the two parameters of (2) is smaller than the experimental error.

* Association (1) is not the only diene synthesis the kinetics of which have been investigated in different solvents. Kaufmann and Wassermann (J., 1939, 870) reported experiments relating to the dimerisation of *cyclo*pentadiene, but in this case the solvent effects were not large enough to produce changes of A and E exceeding the experimental errors.

The initial stage of the trichloroacetic acid catalysis of (1) in benzene solution is kinetically of the third order (cf. preceding paper); for the present purpose, however, the rate is not characterised by third-order catalytic velocity coefficients, v_c, but by second-order velocity coefficients, v, which relate to the overall process (catalysed + non-catalysed association) and are given by $v = v_c c + v_{\text{non-catalysed}}$, where c is the stoicheiometric concentration of the trichloroacetic acid; the velocity coefficient and the non-exponential A factor in the first line of Table I relate to $c = 0{\cdot}0100$ g.-mol./l., *viz.*, to the highest catalyst concentration at which experiments were carried out.

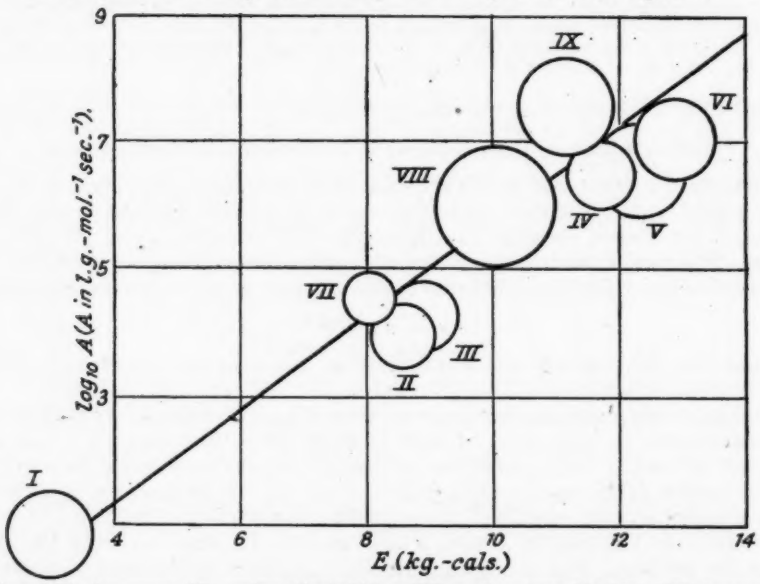
TABLE I.

Catalysis and solvent influence in the formation of cyclo*pentadiene–benzoquinone.*

Measurements in	v (20°).	E.	$\log_{10} A$.	Temp. range.	No. of temps.	No. of runs.
$C_6H_6 + CCl_3{\cdot}CO_2H$	0·03	3·0 ± 1·4	0·9 ± 0·9	13—53°	5	12
CS_2	0·0052	8·5 ± 0·6	4·0 ± 0·6	3—39	7	14
CCl_4	0·0052	8·8 ± 0·4	4·3 ± 0·3	2—50	13	17
C_6H_6	0·0067	11·6 ± 0·4	6·5 ± 0·3	8—50	10	18
n-C_6H_{14}	0·0029	12·1 ± 1	6·5 ± 0·8	20—50	4	12
EtOH	0·030	12·7 ± 0·8	7·0 ± 0·6	2—39	6	9
PhCN	0·048	8·0 ± 0·3	4·5 ± 0·2	10—50	6	6
$PhNO_2$	0·014	10·0 ± 1·2	6·0 ± 1·0	7—50	11	16
$CH_3{\cdot}CO_2H$	0·22	11·0 ± 1	7·5 ± 0·9	10—30	3	6

The parameters E and A in lines 3, 4, and 8 of the table are means of two independent investigations (Fairclough and Hinshelwood; Wassermann; *locc. cit.*); the activation energies and A factors in line 7 were taken

Functional relationship between the parameters of the velocity coefficient.



I, *Trichloroacetic acid in benzene;* II, *carbon disulphide;* III, *carbon tetrachloride;* IV, *benzene;* V, *hexane;* VI, *ethyl alcohol;* VII, *benzonitrile;* VIII, *nitrobenzene;* IX, *acetic acid.*

from Fairclough and Hinshelwood and all the other figures have been deduced from measurements described in the preceding communications of this series or in the experimental part of this paper. v and A are in terms of g.-mols. and secs., and E in kg.-cals. The suggested linear functional relationship between the figures in cols. 3 and 4 is represented in the figure, the magnitude of the experimental errors being indicated by the diameters of the various circles. The slope of the graph is about 10^{-4} cals.$^{-1}$.

In attempting to explain this correlation between the parameters of equation (2), reference is made to the following fundamental equation of the theory of absolute reaction rates (cf. Evans and Polanyi, *Trans. Faraday Soc.*, 1935, **31**, 890; Wynne-Jones and Eyring, *J. Chem. Physics*, 1935, **3**, 492; Eyring, *Chem. Rev.*, 1941, **28**, 308; Laidler, Glasstone, and Eyring, " Theory of Rate Processes," New York, 1941):

$$v = \kappa(kT/h)K^* \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where κ is the transmission coefficient and the factor K^* relates to the equilibrium

$$cyclo\text{Pentadiene } (a) + \text{Benzoquinone } (b) = \text{Activated complex } (t) \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and is defined by

$$K^* = N_t/N_a N_b \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where N_a and N_b are the number of the reactants per unit volume and N_t is the number of the activated complexes per unit volume and per area h in the phase plane of the reaction co-ordinate and its conjugate momentum. It was stated in the preceding paper that the van't Hoff–Dimroth equation connects the constant of an ordinary chemical equilibrium with the solubilities of both reactants and product molecules. According to Evans and Polanyi and Wynne-Jones and Eyring (*locc. cit.*), a similar correlation exists between the equilibrium factor K^* of the rate equation (3) and the solubilities of the initial state and of the activated complex; it is possible, therefore, to deduce a relationship between the velocity coefficients, the transmission coefficient, and the solubilities, σ, of the participants of such equilibria as (4). For the present purpose this relationship can be written as follows

$$v^m\kappa^n/v^n\kappa^m = \sigma_a^m\sigma_b^m\sigma_t^n/\sigma_t^m\sigma_a^n\sigma_b^n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Here and below, the superscripts m and n indicate that the relevant quantities refer either to the various pure solvents or to the benzene solution containing the catalyst, and the subscripts a, b, and t relate respectively to *cyclo*pentadiene, benzoquinone, and to the activated complex. The solubilities of these three molecular species can be represented by

$$\sigma_a = (N_a)^{gas}(N_a)^{solution} = e^{\Delta S_a/R}e^{-\lambda_a/RT} = C_a e^{-\lambda_a/RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

with precisely analogous expressions for σ_b and σ_t, where ΔS and λ are respectively the entropies and heats of solution. Upon substituting the velocity coefficients and the solubilities in (6) by products of non-exponential and exponential factors [using (2), (7), and the corresponding expressions for σ_b and σ_t], a relationship of the same form as equation (6) in the preceding paper can be obtained. If it is assumed that within a small temperature range the parameters A, E, C, and λ do not measurably alter with temperature and that κ^n and κ^m in (6) are equal, then it follows that

$$\log A^m - \log A^n = \log C_t^n + \log C_a^m + \log C_b^m - \log C_t^m - \log C_a^n - \log C_b^n \quad . \quad . \quad . \quad (8)$$

$$E^m - E^n = \lambda_t^n + \lambda_a^m + \lambda_b^m - \lambda_t^m - \lambda_a^n - \lambda_b^n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

The correlation between the non-exponential and the exponential factors of the solubilities (cf. references in preceding paper) can be written in the following form

$$\log C_a^m - \log C_a^n = r(\lambda_a^m - \lambda_a^n) + q_a \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

with analogous expressions for $\log c_b^m - \log c_b^n$ and for $\log c_t^m - \log c_t^n$.

In view of the observations of Evans and Polanyi (see preceding paper), it is assumed that equation (10) and the two analogous expressions with $r \sim 10^{-4}$ cals.$^{-1}$, apply to the participants of such equilibria as (4). The terms on the right-hand side of (10) and its analogues can be substituted, therefore, for those on the right-hand side of (8), leading to

$$\log A^m - \log A^n = r(\lambda_t^n + \lambda_a^m + \lambda_b^m - \lambda_t^m - \lambda_a^n - \lambda_b^n) + (q_a + q_b - q_t) \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Taking (9) into account, we obtain

$$\log A^m - \log A^n = r(E^m - E^n) + (q_a + q_b - q_t) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

which is the suggested functional relationship between the logarithm of the non-exponential A factor of the rate equation (2) and the activation energy.

Experimental.

Benzoquinone, *cyclo*pentadiene, and their addition compound were purified as described in J., 1935, 828. The rate measurements in hexane, carbon disulphide, carbon tetrachloride, nitrobenzene, and acetic acid were carried out in at least two different specimens of each solvent, which was carefully purified by fractional distillation or crystallisation. A measurable change in the reaction velocity could not be observed, and it is concluded that traces of impurities do not produce effects which contribute to the observed solvent influences.

The kinetics of the diene synthesis were measured by using the same colorimetric method as before (*ibid.*). The molar extinction coefficient, η, of benzoquinone and of the addition product were determined in cells the length of which varied from 1 to 20 cm.; Beer's law was found to hold, and there was no measurable change of η with temperature. Numerical values of η in l./g.-mol. cm. are in Table II. The extinction coefficients of the associated molecule in nitrobenzene and

Table II.

Molar extinction coefficients for filter S_{47} of the Zeiss Stufenphotometer.

Solvent.	CS_2.	CCl_4.	$PhNO_2$.	$CH_3{\cdot}CO_2H$.	C_6H_{14}.
Benzoquinone	25·5	16·6	16·3	11·5	13·5
*cyclo*Pentadiene–benzoquinone	0·100	0·0700	0·0434	0·0731	0·0809

acetic acid had to be determined immediately after dissolution, since in these solvents decomposition into the components and subsequent formation of di*cyclo*pentadiene–benzoquinone is much more rapid than in the other solvents. This has to be taken into account in determining the extinction coefficients but not in determining the velocity coefficients, because under the conditions of the kinetic measurements the concentrations are lower.

It has already been stated that those A and E values in Table I which relate to carbon tetrachloride, benzene, and nitrobenzene solution are means of two sets of measurements. The relatively large discrepancies in nitrobenzene solution are possibly due to the fact that this solvent reacts with the product of diene synthesis (1) (cf. Bergmann, *J. Amer. Chem. Soc.*, 1942, **64**, 176), giving rise to the formation of a catalytically active substance, the amount of which would be dependent on concentration or temperature conditions. In carrying out rate measurements in hexane as solvent, it was

found that a solution of benzoquinone decomposes in diffuse daylight but not in the light of the photometer lamp. The results of typical rate measurements are in Table III, the second-order velocity coefficients relating to l., g.-mol., and mins.

In each of the solvents referred to in Table III, a number of runs were carried out in which at a given temperature the initial concentration of the reactants was varied. The conclusion that the rate of the formation of *cyclo*pentadiene–

TABLE III.

Addition of cyclo*pentadiene to benzoquinone in various solvents. Typical experiments.*

(1) = CS_2; (2) = CCl_4; (3) = $PhNO_2$; (4) = AcOH; (5) = n-C_6H_{14}.
Temp.: (1), 3·1°; (2), 40·2°; (3) and (5), 20·4°; (4), 30·0°.
Equimolar initial concns. (g.-mols./l.): (1), 0·0150; (2), 0·0100; (3), 0·00700; (4), 0·00100; (5), 0·0200.

Expt. (1).			Expt. (2).			Expt. (3).			Expt. (4).			Expt. (5).		
Time, mins.	η, cm.$^{-1}$.	v.	Time, mins.	η, cm.$^{-1}$.	v.	Time, mins.	η, cm.$^{-1}$.	v.	Time, mins.	η, cm.$^{-1}$.	v.	Time, mins.	η, cm.$^{-1}$.	v.
25	0·363	0·14	6	0·159	0·74	26	0·0993	0·88	18	0·00795	23	42	0·240	0·15
63	0·340	0·12	31	0·136	0·72	41	0·0930	0·87	25	0·00735	22	86	0·217	0·14
91	0·320	0·14	53	0·118	0·78	65	0·0849	0·79	29	0·00688	23	155	0·182	0·16
122	0·305	0·14	113	0·0919	0·73	104	0·0734	0·79	63	0·00445	26	263	0·149	0·16
185	0·287	0·12	185	0·0705	0·75	140	0·0604	0·77	79	0·00386	26	469	0·108	0·16
309	0·238	0·13	—	—	—	200	0·050	0·94	—	—	—	—	—	—
487	0·202	0·12	—	—	—	—	—	—	—	—	—	—	—	—
700	0·165	0·13	—	—	—	—	—	—	—	—	—	—	—	—

benzoquinone can be characterised by second-order velocity coefficients is based on the facts that in individual runs no systematic trend could be observed, and that at various initial concentrations consistent second-order velocity coefficients are obtained which agree within the limits of the experimental error.

The receipt of research grants from the Central Research Fund and from the Chemical Society is gratefully acknowledged.

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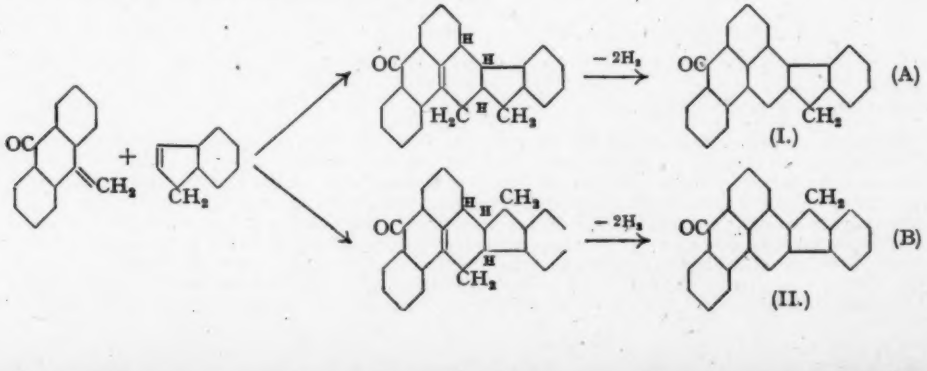
130. *Indeno-2″ : 3″ : 2′ : 1′-benzanthrone.*

By G. SWAIN and A. R. TODD.

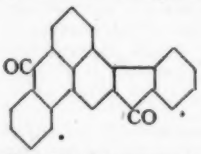
Indeno-2″ : 3″ : 2′ : 1′-benzanthrone and a *dihydroindeno-2″ : 3″ : 2′ : 1′-benzanthrone* have been prepared by the reaction of indene with methyleneanthrone in nitrobenzene solution. Oxidation of both products gave *1″-ketoindeno-2″ : 3″ : 2′ : 1′-benzanthrone*, the structure of which has been determined by an alternative synthesis from ethyl cinnamate and methyleneanthrone.

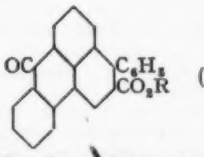
THE marked tumour-inhibitory properties of 1 : 2 : 5 : 6-dibenzfluorene (Haddow and Robinson, *Proc. Roy. Soc.*, 1939, *B*, **127**, 277) lends interest to the preparation and examination in this sense of other readily accessible complex fluorene derivatives. Concurrently with the work on this hydrocarbon (Swain and Todd, J., 1941, 674) we synthesised for this purpose *indeno-2″ : 3″ : 2′ : 1′-benzanthrone* (I).

The synthesis of benzanthrone derivatives by the Diels–Alder reaction with methyleneanthrone, or methylene-substituted methyleneanthrones, as the diene component has been demonstrated by Clar (*Ber.*, 1936, **69**, 1686; D.R.-P. 619,246; cf. also I. G. Farbenindustrie A.-G., D.R.-P., 591,496, 597,325), using maleic anhydride, cinnamic acid, benzoquinone and similar compounds as active olefin components. Alder and Rickert (*Ber.*, 1938, **71**, 379) found that indene undergoes 1 : 4 addition to 2 : 3-dimethylbutadiene and *cyclo*pentadiene. It thus appeared that indene might condense with methyleneanthrone to an indenobenzanthrone according to scheme (A) or (B). If the reaction proceeded according to (B), the product (II) on oxidation would yield 1″-ketoindeno-3″ : 2″ : 2′ : 1′-benzanthrone, a probable by-product in the preparation of dibenzpyrenequinone from 1 : 5-dibenzoylnaphthalene (I. G. Farbenindustrie A.-G., D.R.-P. 426,710, 1923; *Chem. Zentr.*, 1936, II, 653). On general grounds, however, scheme (A) seemed the more likely mode of reaction and, in fact, this has been confirmed experimentally.



Methyleneanthrone and indene, heated together in nitrobenzene solution, gave a mixture of indeno-2″ : 3″ : 2′ : 1′-benzanthrone (I) and a *dihydroindeno-2″ : 3″ : 2′ : 1′-benzanthrone* in yields of 15% and 31% respectively. In benzene or xylene solution, only the dihydro-compound was obtained but in lower yield; by heating with nitrobenzene, it was dehydrogenated in part to indeno-2″ : 3″ : 2′ : 1′-benzanthrone. That the product obtained in larger quantity was a dihydro- and not a tetrahydro-indenobenzanthrone was proved by dehydrogenation with palladised charcoal, only one mol. of hydrogen being obtained; the location of the two extra hydrogen atoms in the dihydro-compound remains uncertain.

(III.) 



(IV.)

Both indeno-2″ : 3″ : 2′ : 1′-benzanthrone and its dihydro-derivative have been converted into *1″-keto-indeno-2″ : 3″ : 2′ : 1′-benzanthrone* (III) in almost quantitative yield by oxidation with selenious acid, although separation of the ketone from selenium proved rather troublesome. The fact that no vat could be obtained from either the indenobenzanthrone or the ketoindenobenzanthrone was an indication that diene synthesis had occurred in the manner illustrated in (A). The ketoindenobenzanthrone would then possess an odd number of carbon atoms in the chain linking the two carbonyl groups, whereas if it had the structure related to (II) it would possess an even number of carbon atoms and should therefore vat. The constitution, however, was firmly established by independent synthesis from methyleneanthrone and ethyl cinnamate. Heated together in nitrobenzene solution, these compounds yielded two esters, both of which gave on hydrolysis *1′-phenylbenzanthrone-2′-carboxylic acid* (IV; R = H). Although interconversion was not achieved, it would seem probable that they represent dimorphs of *ethyl 1′-phenylbenzanthrone-2′-carboxylate* (IV; R = Et), formed by dehydrogenation of the initial adduct by the nitrobenzene employed as solvent. The structure of the parent acid was proved by decarboxylation to 1′-phenylbenzanthrone, which, as Clar (*loc. cit.*) has shown, results directly from the reaction between cinnamic acid and methyleneanthrone in nitrobenzene. Ring closure of 1′-phenylbenzanthrone-2′-carboxylic acid to 1″-ketoindeno-2″ : 3″ : 2′ : 1′-benzanthrone, identical with the specimen previously prepared, was readily effected by sulphuric acid.

In the above experiments the formation of a dihydroindenobenzanthrone as sole product when the diene synthesis was carried out in xylene or benzene was surprising even if the initially formed tetrahydro-derivative might be expected to be rather unstable; no exactly analogous case has come to our notice. It is, of course, known that nitrobenzene used as a solvent in diene synthesis can effect dehydrogenation of newly formed six-membered rings, giving dihydrobenzene (Weizmann, E. Bergmann, and Berlin, *J. Amer. Chem. Soc.*, 1938, **60**, 1331) or fully aromatic nuclei (Clar, *Ber.*, 1936, **69**, 1686; F. Bergmann, *J. Amer. Chem. Soc.*, 1942, **64**, 176). According to F. Bergmann (*loc. cit.*) this action of nitrobenzene can only occur in cases where the initial adduct is capable of double ortho-enolisation as in the adducts with quinones or maleic anhydride. While this mechanism may apply to adducts formed with such reagents, and while this enolisation tendency may predispose them to dehydrogenation, it is obvious from the work here described and from that of Clar (*loc. cit.*) that such conditions are not necessary and that the determining factor in other cases may be simply the tendency towards formation of a stable ring system.

In animal experiments carried out by Dr. A. Haddow at the Royal Cancer Hospital, details of which will be published elsewhere, both indeno-2″ : 3″ : 2′ : 1′-benzanthrone and 1″-ketoindeno-2″ : 3″ : 2′ : 1′-benzanthrone showed tumour-inhibitory properties of a moderate order.

Experimental.

Condensation of Methyleneanthrone and Indene.—(a) *In nitrobenzene.* Methyleneanthrone (30 g.), indene (20 g.), and nitrobenzene (75 c.c.) were refluxed for 1½ hours. The solution, on cooling, deposited an orange-yellow crystalline solid (27 g.), which was separated and washed with benzene. The product (27 g.) was refluxed with benzene (750 c.c.) for 1 hour and filtered hot from a yellow solid (A). The filtrate deposited orange needles (10·7 g.), m. p. 207—212°, contaminated with a little of (A). Recrystallisation from benzene yielded *indeno-2″ : 3″ : 2′ : 1′-benzanthrone* (4·4 g.) in orange needles, m. p. 218—219° (Found: C, 90·8; H, 4·65. $C_{24}H_{14}O$ requires C, 90·6; H, 4·4%).

The solid (A) was again extracted with boiling benzene (300 c.c.) for 1 hour, and the undissolved solid recrystallised from xylene. *Dihydroindeno-2″ : 3″ : 2′ : 1′-benzanthrone* separated in yellow prismatic plates (11·0 g.), m. p. 252—253° (Found: C, 90·5; H, 5·2. $C_{24}H_{16}O$ requires C, 90·0; H, 5·0%). Further quantities of pure indeno-2″ : 3″ : 2′ : 1′-benzanthrone (2·6 g.) and its dihydro-derivative (4·0 g.) were obtained from the mother-liquors, and addition of benzene to the nitrobenzene mother-liquors caused slow separation of a little more crude indeno-2″ : 3″ : 2′ : 1′-benzanthrone (3 g. approx.).

(b) *In xylene.* Methyleneanthrone (5 g.), indene (3·5 g.), and xylene (25 c.c.) were refluxed for 2½ hours. The solution rapidly became orange-coloured and a yellow crystalline solid commenced to separate. After cooling, the solid (2·3 g.) was collected, washed with xylene, and recrystallised from the same solvent, dihydroindeno-2″ : 3″ : 2′ : 1′-benzanthrone separating in pale yellow, prismatic plates, m. p. 252—253°, undepressed by the specimen obtained in (a).

(c) *In benzene.* Methyleneanthrone (5 g.), indene (3·5 g.), and benzene (100 c.c.) were refluxed for 18 hours. On cooling, dihydroindeno-2″ : 3″ : 2′ : 1′-benzanthrone (2·0 g.) separated, m. p. 252—253° after crystallisation from xylene, undepressed by specimens from (a) or (b).

Dehydrogenation of Dihydroindeno-2″ : 3″ : 2′ : 1′-benzanthrone.—(a) *By nitrobenzene.* The substance (1·0 g.), refluxed for 4 hours with nitrobenzene (10 c.c.), yielded an orange crystalline solid (0·7 g.) on cooling. This was extracted with boiling benzene (*ca.* 25 c.c.), and the sparingly soluble unchanged dihydro-compound removed; the filtrate, after cooling, was decanted from the first deposited dihydro-compound and, on standing, gave orange needles (0·15 g.).

Recrystallisation from benzene yielded indeno-2″ : 3″ : 2′ : 1′-benzanthrone (0·1 g.), m. p. 217—219°, undepressed by that previously obtained.

(b) *By palladised charcoal.* The compound (0·41 g.), m. p. 252—253°, was heated at 270° in an inert atmosphere with palladium–charcoal (0·2 g.), the temperature being raised to 310° as the gas evolution ceased. The volume of hydrogen collected was 24·5 c.c. at N.T.P. (calc. for dihydro-compound, 28·7 c.c.). The product was again indeno-2″ : 3″ : 2′ : 1′-benzanthrone.

1″-Ketoindeno-2″ : 3″ : 2′ : 1′-benzanthrone.—Dihydroindeno-2″ : 3″ : 2′ : 1′-benzanthrone (4 g.), selenium dioxide (8 g.), and water (8 c.c.) were heated together in a sealed tube for 4½ hours at 230°. The resultant red-brown crystalline solid (5·2 g.) was washed with water, dried in the steam oven, and extracted (Soxhlet) with xylene. The solid was still contaminated with selenium, most of which was removed by sublimation at 150—180°/*ca.* 0·0001 mm. The ketone sublimed readily at about 280° and was recrystallised from nitrobenzene. *1″-Ketoindeno-2″ : 3″ : 2′ : 1′-benzanthrone* (3·0 g.) separated in red needles, m. p. 336—338° (Found : C, 86·4; H, 4·0. $C_{24}H_{12}O_2$ requires C, 86·7; H, 3·6%).

1″-Ketoindeno-2″ : 3″ : 2′ : 1′-benzanthrone was also obtained from indeno-2″ : 3″ : 2′ : 1′-benzanthrone by an exactly similar oxidation; it is, therefore, unnecessary to separate the mixture obtained from the reaction between indene and methyleneanthrone if the ketone is desired as the final product.

Condensation of Ethyl Cinnamate and Methyleneanthrone.—Methyleneanthrone (5 g.), ethyl cinnamate (5·0 g.), and nitrobenzene (10 c.c.) were refluxed for 1½ hours, and alcohol (50 c.c.) added to the cooled, dark brown solution. After 12 hours the crystalline solid (3·0 g.) was removed, and alcohol (50 c.c.) added to the filtrate; more solid slowly separated (1·5 g.). The combined solids were fractionally crystallised from ethyl acetate. *Ethyl 1′-phenylbenzanthrone-2′-carboxylate* separated in golden yellow prismatic plates (2·0 g.), m. p. 155—156° (Found : C, 82·6; H, 4·8. $C_{26}H_{18}O_2$ requires C, 82·5; H, 4·8%), accompanied by a smaller amount of a second *ester* crystallising in clusters of very small, yellow needles, m. p. 190—210° (Found : C, 81·9; H, 4·5. $C_{26}H_{18}O_2$ requires C, 82·5; H, 4·8%).

1′-Phenylbenzanthrone-2′-carboxylic Acid.—A solution of ethyl 1′-phenylbenzanthrone-2′-carboxylate (1·0 g.) in alcohol (50 c.c.) was refluxed with alcoholic potash (4 g. of potassium hydroxide, 4 c.c. of water, 20 c.c. of alcohol) for 1½ hours; water (100 c.c.) was then added to give a clear orange solution. The yellow flocculent precipitate (0·95 g.) obtained by acidification with hydrochloric acid was collected, washed with water, and crystallised from acetic acid, *1′-phenylbenzanthrone-2′-carboxylic acid* separating as a felted mass of yellow needles, m. p. 284—286° (Found : C, 82·3; H, 4·0. $C_{24}H_{14}O_2$ requires C, 82·3; H, 4·0%). Hydrolysis of the ester, m. p. 190—210°, by the above method gave the same 1′-phenylbenzanthrone-2′-carboxylic acid.

1′-Phenylbenzanthrone.—The acid (0·5 g.), m. p. 284—286°, was refluxed for 1 hour with quinoline (5 c.c.) and copper bronze (50 mg.), methyl alcohol added, and the yellow needles (0·35 g., m. p. 182—184°) collected, washed with a little methyl alcohol, and recrystallised from ethyl acetate. 1′-Phenylbenzanthrone separated in yellow needles, m. p. 182—183° (Found : C, 90·2; H, 4·5. Calc. for $C_{23}H_{14}O$: C, 90·2; H, 4·6%), undepressed by a specimen, m. p. 185—186°, prepared from cinnamic acid and methyleneanthrone according to the method of Clar (*loc. cit.*).

Ring-closure of 1′-Phenylbenzanthrone-2′-carboxylic Acid.—The acid (0·4 g.) was heated on the steam-bath for 30 mins. with sulphuric acid (4·5 c.c., *d* 1·84, diluted with 0·5 c.c. of water). The colour changed from cherry-red to greenish-violet. Ice was added, and the red precipitate collected, washed with water, and dried (0·3 g.). Crystallisation from nitrobenzene yielded red needles of 1″-ketoindeno-2″ : 3″ : 2′ : 1′-benzanthrone, m. p. 336—338°, undepressed by a specimen prepared by oxidation of indeno-2″ : 3″ : 2′ : 1′-benzanthrone.

The authors thank I.C.I. (Dyestuffs) Ltd. for their support of this investigation.

UNIVERSITY OF MANCHESTER. [*Received, July 9th,* 1942.]

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131. Cannabis Indica. *Part XI. An Examination of the Alkali-soluble Portion of American Hemp Resin.*

By (MRS.) A. MADINAVEITIA, P. B. RUSSELL, and A. R. TODD.

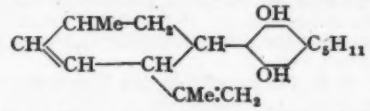
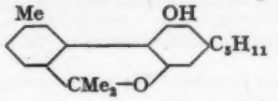
The alkali-soluble portion of the resin extracted from American wild hemp (marihuana) can be separated into two components, one of which can and the other cannot be extracted from alkaline solution with ether. These materials, on boiling with methyl alcohol, or better on standing with alkali, yield alkali-insoluble resins, from which cannabidiol and cannabinol respectively have been isolated. On the evidence presented it is concluded that the alkali-soluble portion of the resin contains esters of cannabidiol and cannabinol with a phenolic acid. This conclusion is supported by the properties of synthetic esters of these compounds with *p*-hydroxybenzoic acid.

IN the latter part of 1939 we were privileged, through the courtesy of Mr. F. Thornton, of the Home Office, and of Mr. H. J. Anslinger of the U.S. Bureau of Narcotics, to read a report submitted to the latter by an American chemist dealing with the alkali-soluble portion of the resin from American hemp (marihuana). The findings in this report were of great interest to us, since, although alkali-solubility had been reported occasionally in the past for a part of the physiologically active resin from *Cannabis* (cf. *e.g.*, Hoffmann-La Roche, D.R.P. 285,829, 1913), no alkali-soluble components other than minor amounts of fatty acids, etc., had been found in any samples of Indian or Egyptian resin examined in these laboratories. This of course may have been due to the fact that our starting materials were always Oriental prepared drugs (ganja or hashish), which might well have undergone various changes after collection from the plant sources. Through the kindness of Mr. H. J. Anslinger, to whom our sincere thanks are due, we were supplied in the early summer of 1940 with a small amount of marihuana; from it we extracted the active resin and examined its properties in the light of the above-mentioned report. Our results obtained at that time we refrained from making public until the American chemist published his original observations; this has now been done [Fulton, *Ind. Eng. Chem.* (*Anal.*), 1942, **14**, 407] and our findings, which amplify them in several important respects, are now recorded.

To make the general position as established by Fulton (*loc. cit.*) clear, it is necessary to summarise his findings briefly. He found that a portion of the undistilled hemp resin could be extracted from light petroleum solution with dilute aqueous sodium hydroxide. The alkali-soluble material could itself be separated into two distinct resinous fractions : (*a*) " Cannabinol IRAB," which could not be extracted from alkaline solution with

ether and gave a positive reaction (purple colour) in the alkaline Beam test (4th Report, Wellcome Trop. Res. Lab., Khartoum, 1911, *B*, 25), and (*b*) " cannabinol INRAB," extractable from alkaline solution with ether and giving no coloration in the Beam test. These two resins, on refluxing with methyl alcohol, gradually changed, yielding alkali-insoluble resins whose other properties remained similar to those of the originals. These products were described by him respectively as " cannabinol IIRAB " and " cannabinol IINRAB " and it was tentatively suggested on the basis of colour reactions that they might be identical with cannabidiol (I) and cannabinol (II), both well-known constituents of *Cannabis* resins, although no satisfactory explanation was given of the reactions involved in the various changes.

On extracting the resin from the sample of marihuana at our disposal and performing the alkali separations described by Fulton (*loc. cit.*), we readily obtained the products IRAB and INRAB (for convenience we omit the prefaced " cannabinol," which is in any event misleading) and confirmed their conversion into IIRAB and IINRAB on prolonged boiling with methyl alcohol. This behaviour seemed to us most readily explained on the assumption that IRAB and INRAB contained esters of cannabidiol and cannabinol respectively with some phenolic acid conferring alkali-solubility, and that on heating with methyl alcohol methanolysis occurred, liberating cannabidiol (IIRAB) and cannabinol (IINRAB), which are alkali-insoluble and show the appropriate behaviour in the alkaline Beam test. On this view IRAB and INRAB would conform in type to the depside class of natural products, esters which in many cases undergo fission on heating with methyl alcohol. It is perhaps of some significance in this connection that both cannabidiol and cannabinol may be regarded as derivatives of olivetol (5-*n*-amylresorcinol), a well-known constituent of natural depsides (*e.g.*, olivetoric acid), in which it occurs esterified with phenolic acids. In accordance with this view the strong green ferric chloride reaction of IRAB and INRAB was not given by the alkali-insoluble resins prepared by heating with methyl alcohol, but it remained a property of the alkali-soluble portion of the reaction products. Again, it was found that the conversions IRAB ⟶ IIRAB and INRAB ⟶ IINRAB could be brought about rather more easily by standing with sodium hydroxide. From IIRAB prepared in this way we isolated cannabidiol as its 3 : 5-dinitrobenzoate (Adams, Hunt, and Clark, *J. Amer. Chem. Soc.*, 1940, **62**, 196) and from IINRAB cannabinol as its *p*-nitrobenzoate (Work, Bergel, and Todd, *Biochem. J.*, 1939, **33**, 123), although neither could be isolated from IRAB or INRAB before alkali treatment. The alkali-soluble products of the conversion in each case contained an acid giving a strong green ferric reaction. Unfortunately we were unable with the amount at our disposal to characterise this acid, but it resembled protecatechuic acid closely in its reactions.

(I.)  (II.) 

Since lack of marihuana precluded further study of the above phenolic acid, confirmatory evidence for our hypothesis was sought in another way. *Cannabinol* p-*carbomethoxybenzoate* and *cannabidiol bis*-p-*carbomethoxybenzoate* (the latter in a somewhat impure condition) were prepared and partially hydrolysed under conditions designed to remove only the carbomethoxy-group and yield the corresponding *p*-hydroxybenzoates. The products, both resinous, showed, apart of course from the ferric reaction, exactly similar properties to the alkali-soluble fractions of the resin from marihuana. Thus the product from cannabidiol, like IRAB, was soluble in alkali and could not be extracted from alkaline solution with ether, whereas the cannabinol derivative, although also soluble in alkali, could, like INRAB, be extracted from alkaline solution with ether. Like IRAB and INRAB, too, they gave respectively cannabidiol and cannabinol on boiling with methyl alcohol or standing with alkali. In view of these findings there can be little doubt that, in American hemp at least, cannabidiol and cannabinol occur in part esterified with some phenolic acid or acids and that in this form they are alkali-soluble. The extent to which they occur in this form may well vary considerably in different samples of hemp.

In the course of the present investigation we took the opportunity to have the various marihuana fractions examined for hashish activity, using the Gayer test on rabbits. The results, which are recorded in the experimental section, show that the alkali-soluble portion of the resin has at most very little activity, and that the physiologically active material is mainly found, as in the Oriental drugs, in one high-boiling fraction of the alkali-insoluble resin. From this active fraction we isolated a quantity of cannabidiol as its 3 : 5-dinitrobenzoate, but were unable to isolate cannabinol as its *p*-nitrobenzoate, although this procedure is satisfactory in the case of Indian and Egyptian active resins (Work, Bergel, and Todd, *loc. cit.*; Jacob and Todd, J., 1940, 649). Failure to isolate cannabinol from marihuana by this method has already been reported by Adams and his collaborators (*loc. cit.*). The absence of any marked physiological activity in the alkali-soluble portion of the resin explains, of course, the apparent lack of correlation between the proportion of this material and the potency of drugs from different sources. Since the physiological activity of hemp resins appears, on available evidence, to be due to the presence of a mixture of tetrahydrocannabinols, it seems not unreasonable to expect that in some cases the active compounds might also exist in the form of depsides. This might explain the occasional reports of the value of extraction with alkali in concentrating hemp preparations.

Experimental.

Preparation of the Resin.—The starting material (1435 g.), consisting of the dried flower tops and leaves of American hemp, was percolated with light petroleum (b. p. 40—60°); the petroleum extract on evaporation yielded a dark brown resin (67 g.).

Alkali-soluble Portion of the Resin: IRAB and INRAB.—The above resin (63 g.), dissolved in light petroleum, was extracted rapidly with sodium hydroxide solution (2%) containing *ca.* 2% of sodium sulphite to prevent oxidation (cf. Fulton, *loc. cit.*). The alkali-insoluble portion was recovered from the petroleum layer by evaporation (41 g.). From the purple alkaline solution, INRAB (3·4 g.) was obtained by ether extraction; this product, a brownish resin, gave a feeble colour in the alkaline Beam test (probably due to traces of IRAB) and a strong green ferric reaction. IRAB (13 g.) was obtained from the residual alkaline solution by acidification and extraction with light petroleum; it showed a strong green ferric reaction and was strongly positive in the alkaline Beam test.

Conversion of IRAB into IIRAB and INRAB into IINRAB.—IRAB (0·25 g.) was refluxed with methyl alcohol (30 c.c.) for 6 hours, the solution evaporated, and the residue extracted with light petroleum. After separation from insoluble matter (0·1 g.) the solution was treated with alkali as in the original separation; the resin (0·12 g.) was now alkali-insoluble (IIRAB). In exactly similar fashion INRAB was converted into IINRAB. In both cases IIRAB and IINRAB gave no coloration with ferric chloride, but the alkali-soluble portion of the reaction products gave a deep green coloration.

Hydrolysis of IRAB with Alkali: Isolation of Cannabidiol.—IRAB (2 g.) was dissolved in the sodium hydroxide–sodium sulphite mixture (18 c.c.) used in the original separation. On standing at room temperature a resin gradually separated; after 2 days this resin was extracted with ether. It had the properties of IIRAB and on treatment with 3 : 5-dinitrobenzoyl chloride it gave cannabidiol bis-3 : 5-dinitrobenzoate, m. p. 105°, undepressed by an authentic sample (m. p. 106—107°) from Egyptian hashish.

The alkaline solution, after removal of IIRAB in this experiment, was acidified and extracted several times with ether. The combined extracts were extracted with sodium bicarbonate solution, the bicarbonate layer being subsequently acidified and again extracted with ether. Evaporation of the ethereal solution gave a small amount of gummy acid which reduced ammoniacal silver nitrate and gave a deep green coloration with ferric chloride. This gum could be made to crystallise by rubbing with a crystal of protocatechuic acid (which shows similar reactions), but the amount obtainable was too small to permit of rigid identification. If the acid in question were indeed protocatechuic acid, most of it would have been lost in the process of working-up owing to high water-solubility.

Hydrolysis of INRAB with Alkali: Isolation of Cannabinol.—The above experiment was repeated with INRAB with similar results. The acid fraction again had the colour reactions of protocatechuic acid. The IINRAB produced was distilled and *p*-nitrobenzoylated. The crude ester, dissolved in methyl alcohol–methyl acetate and allowed to cool, yielded yellowish needles. Recrystallised from alcohol, they had m. p. 161—162°, undepressed by cannabinol *p*-nitrobenzoate (m. p. 161—162°).

Alkali-insoluble Portion of Hemp Resin.—That portion (41 g.) of the original resin which was not extractable from light petroleum solution with alkali was dissolved in warm methyl alcohol (500 c.c.); a crystalline hydrocarbon (12 g.) (assumed to be nonacosane by analogy with other hemp resins) slowly separated. The solution was evaporated, and the residual resin distilled under *ca.* 10^{-4} mm., the following fractions being obtained (all temps. are bath temp.): (i) Up to 108° (3 g.), Beam, −ve; (ii) 110—130° (5 g.), Beam, +ve; (iii) 130—150° (5 g.), Beam, faintly +ve; (iv) residue, 16 g. Fraction (ii) contained virtually all the physiologically active material; it was *p*-nitrobenzoylated and chromatogrammed on aluminium oxide, a solid ester, m. p. *ca.* 70°, being obtained. This on hydrolysis and re-acylation with 3 : 5-dinitrobenzoyl chloride gave cannabidiol bis-3 : 5-dinitrobenzoate, m. p. 105—106°. From the residual oily *p*-nitrobenzoates no cannabinol derivative crystallised; they contained the active material and were practically Beam negative.

Pharmacological Test Results.—We are indebted to Professor A. D. Macdonald of this University for the following results (Gayer test):

1 Total light petroleum extract of marihuana. Active at 5 mg./kg.
2 Alkali-insoluble portion of above extract. Active down to 1 mg./kg.
3 IRAB
4 INRAB
5 IIRAB
6 IINRAB
} Inactive at 5 mg./kg.
7 Fraction (ii) of distilled alkali-insoluble resin. Active at 1 mg./kg.

Cannabinol p-Carbomethoxybenzoate.—Cannabinol (0·3 g.) was dissolved in pyridine (1 c.c.), *p*-carbomethoxybenzoyl chloride (0·2 g.) (Fischer, *Ber.*, 1908, **41**, 2878) added, and the mixture heated for several hours on the steam-bath and left overnight. On pouring into water and acidifying with hydrochloric acid a brownish precipitate separated; it was washed with sodium bicarbonate solution and water and purified by repeated precipitation from chloroform solution with methyl alcohol. The product was a white powder, m. p. 195°, of doubtful crystalline nature (Found in material dried at 120°: C, 73·5; H, 6·6. $C_{30}H_{32}O_6$ requires C, 73·8; H, 6·6%).

The above *ester* (0·75 g.) was mixed with N-potassium hydroxide (50 c.c.) and left at room temperature for 30 minutes; the mixture was then acidified and extracted with ether, and the extract washed with bicarbonate solution. Evaporation of the dried extract yielded a brownish resin. This was dissolved in light petroleum and the alkali separation of Fulton (*loc. cit.*) applied to the solution. A certain amount of the resin (0·3 g.) was insoluble in alkali (presumably owing to the hydrolysis of the carbomethoxy-ester having in part gone too far, yielding cannabinol), but the remainder (0·2 g.) was, like INRAB, soluble in alkali but extractable from alkaline solution with ether. The latter portion on refluxing with methyl alcohol for 5 hours was largely converted into an alkali-insoluble resin like IINRAB. A small amount remained unaffected at the end of this time; apparently the *p*-hydroxybenzoate of cannabinol is rather more resistant to methanolysis than INRAB.

Cannabidiol Bis-p-carbomethoxybenzoate (?).—Esterification of cannabidiol (2 g.) with *p*-carbomethoxybenzoyl chloride (2 g.) in pyridine (20 c.c.) was carried out as above. The product was a brownish resin which could not be obtained in solid form. It distilled at *ca.* 130—150° (bath temp.)/10^{-3} mm. but gave unsatisfactory analytical values (Found: C, 65·0; H, 6·4. $C_{39}H_{42}O_{10}$ requires C, 69·9; H, 6·4%). As it probably consisted mainly of the desired ester, it was used directly for further work.

The resin (1 g.) was partially hydrolysed under nitrogen by N-sodium hydroxide (30 c.c.) for 30 minutes. The product (0·5 g.), subjected as above to the alkali separation, gave in addition to some alkali-insoluble material (0·3 g.) a resin (0·1 g.) which, like IRAB, was soluble in alkali, not extractable from alkaline solution with ether, and on prolonged boiling with methyl alcohol was converted into an alkali-insoluble product just as IRAB can be converted into IIRAB.

The authors thank Messrs. Roche Products, Ltd., for a grant held by one of them (A. M.).

THE UNIVERSITY, MANCHESTER. [*Received, July 28th,* 1942.]

132. *Some Further Observations on the Interchange of Heavy Oxygen between Water and Certain Inorganic Oxy-anions.*

By E. R. S. Winter and H. V. A. Briscoe.

Using heavy-oxygen water having an excess density due to ^{18}O of 150—210γd, the study of the interchange of oxygen between water and oxyacid radicals has been extended, with particular reference to the interchange of the sulphate and bisulphate ion. This work arose from observations previously published (Winter, Carlton, and Briscoe, J., 1940, 131) wherein some puzzling aspects of such interchanges were revealed. Two of the observations recorded in the above paper require amendment, since it has now been found that potassium hydrogen sulphate and potassium dihydrogen orthophosphate do interchange, though slowly, at 100°. The interchange of potassium hydrogen sulphate has been examined for concentrations ranging from 1·226 to 6·13M at 100°, and in 3·85 and 6·13M-solutions at 108°. The interchange of the sodium salt has been studied at 100° in 6·13 and 3·85M-solutions. In certain cases the effect of the addition of other salts and of free acid has also been examined. The results of all the experiments now reported are given in Tables I and II, and the more important of them are plotted in Fig. 1. It is established that the rate of interchange in bisulphate solutions increases with concentration, and with temperature; that the nature of the cation exerts a marked influence on the rate of interchange, which is substantially greater with the sodium than with the potassium salt; and that the addition of other (inert) salts or of free acid to the system also increases the rate of interchange. It is also apparent that the rate of interchange for potassium dihydrogen orthophosphate is substantially lower than that for potassium hydrogen sulphate.

Analysis of the results shows that no simple mechanism will satisfactorily explain the experimental figures, and it is concluded that the most probable explanation is that interchange occurs through anhydride formation. This statement is shown also to apply to the interchange with potassium dihydrogen orthophosphate at 100° and with potassium chromate at 20°.

Various theories have been proposed to account for the interchange of oxygen between water and inorganic compounds. Datta, Day, and Ingold (J., 1937, 1968) put forward three possibilities: (1) Dehydration followed by hydration; this seems to be the mechanism whereby silicates, borates, and possibly chromates suffer interchange (Winter, Carlton, and Briscoe, *loc. cit.*). (2) Hydration followed by dehydration; this has been

Table I.

Heavy oxygen interchange in solutions of acid salts of oxy-acids.

[All experiments were at 100° except where otherwise indicated, and the original heaviness of water due to ^{18}O (γd) is 210 except where annotated.]

Expt. No.	Molarity.	Time (hrs.).	Interchange, %.	$\Delta\gamma d_t$.	$\Delta\gamma d_\infty$.	Expt. No.	Molarity.	Time (hrs.).	Interchange, %.	$\Delta\gamma d_t$.	$\Delta\gamma d_\infty$.
					$KHSO_4$.						
1	6·13	22	47·0	−30	−64	15	2·45	72	35·5	−11	−31
2	,,	45	65·6	−42	,,	16	,,	115	45·1	−14	,,
3	,,	90	86·0	−55	,,	17	,,	194	55·0	−17	,,
4	,,	120	92·2	−59	,,	18	1·226	43	11·8	− 2	−17
5	4·53	14	32·7	−17	−52	19	,,	93	29·4	− 5	,,
6	,,	22	42·3	−22	,,	20	,,	144	35·3	− 6	,,
7	,,	50	60·0	−31	,,	21	,,	186	47·1	− 8	,,
8	,,	136	73·0	−38	,,	22 *	6·13	5	40·0	−23	−58
9	3·85	10	19·6	− 9	−46	23 *	,,	13	72·4	−42	,,
10	,,	20	34·8	−16	,,	24 *	,,	20	88·0	−51	,,
11	,,	45	52·2	−24	,,	25 *	3·85	5	31·7	−13	−41
12	,,	100	60·1	−28	,,	26 *	,,	13	58·5	−24	,,
13	,,	160	63·0	−29	,,	27 *	,,	30	75·6	−31	,,
14	2·45	42	29·0	− 9	−31	28 †	6·13	5	100·0	−59	−58
					$NaHSO_4$.						
29 ‡	6·13	10	41·4	−24	−58	32	3·85	20	41·3	−19	−46
30 ‡	,,	23	62·0	−36	,,	33	,,	45	60·1	−28	,,
31 ‡	,,	46	80·0	−47	,,	34	,,	96	74·0	−34	,,
						35	,,	190	84·8	−39	,,
					KH_2PO_4.						
36 §	2·78	70	29·0	− 9	−31	38 §	2·78	167	45·0	−14	−31
37 §	,,	100	35·5	−11	,,						

* Temperature = 108° and γd = 186. ‡ γd = 186.
† ,, 132° and γd = 186. § γd = 156.

realised by Mills and Urey (*J. Amer. Chem. Soc.*, 1940, **62**, 1019) in the system carbon dioxide–water, and it also most probably plays a part in the interchange of borates (Winter, Carlton, and Briscoe, *loc. cit.*). (3) Temporary covalency increase; this was the mechanism put forward for the interchange observed in alkaline solutions of sodium sulphate, and was also used by Blumenthal and Herbert (*Trans. Faraday Soc.*, 1937, **33**, 849) to explain the interchange they observed in solutions of tripotassium orthophosphate. Titani and Goto (*Bull. Chem. Soc. Japan*, 1939, **14**, 77) examined the interchange of various salts in acid and neutral solutions

TABLE II.

Miscellaneous experiments, mainly on interchange in solutions of mixtures.

[Temp. = 100° except in No. 40, where temp. = 0°. 3 Ml. of water used in each expt.]

Expt. No.	Substance.	Wt. used (g.).	Molarity.	Time, hrs.	Interchange, %.	γd_0.	$\Delta\gamma d_t$.	$\Delta\gamma d_\infty$.
39	H_2SO_4	0·49	1·67	169	100	210	−24	−23
40	"	"	"	<0·5	"	"	−23	−23
41	Na_2SO_4	1·4	3·29	151	48·5	"	−16	−33
	H_2SO_4	0·45	1·53	"	100 *	"	−21 *	−21 *
42	NaClO$_4$	1·0	2·73	210	14·3	"	− 4	−28
	H_2SO_4	0·56	1·71	"	100 *	"	−23 *	−23 *
43	NaHSO$_4$	1·388	3·85	157	100	"	−46	−46
	NaClO$_4$	1·0	2·73	"	13·3 †	"	− 4 †	−30 †
44	NaHSO$_4$	1·388	3·85	100	87·0	"	−40	−46
	NaClO$_4$	1·0	2·73	"	13·3 †	"	− 4 †	−30 †
45	KHSO$_4$	1·574	3·85	21	45·6 ‡	"	−21 ‡	−46 ‡
	KCl	0·25	1·12	"	—	"	—	—
46	KHSO$_4$	1·00	2·45	72	57·1 ‡	186	−16 ‡	−28
	KCl	0·25	1·12	"	—	"	—	—
47	KHSO$_4$	1·00	2·45	70	63·0	"	−17 ‡	−27
	HCl (conc.)	0·3	1·11	"	—	"	—	—
48	$Na_4P_2O_7$	1·5	1·88	41	0	210	0	−40
49	$Na_4P_2O_7$	1·5	1·88	41	2·5 §	"	− 1 §	−40
	NaOH	0·10	0·83	"	100	"	− 3	− 3
50	$Na_4P_2O_7$	1·5	1·88	64	15·0	"	− 6	−40
	H_2SO_4	0·04	0·13	"	100 *	"	− 2 *	− 2 *

* Interchange of the H_2SO_4 assumed here to be 100%, by reason of experiments 39 and 40.

† A value of −4 for $\Delta\gamma d_t$ is here assumed for the interchange of $NaClO_4$, by reason of experiment 42. The balance of the observed decrease in water density is assumed due to interchange of $NaHSO_4$.

‡ These results have been corrected for the amount of NaOH added during the purification of the water.

§ This experiment was performed in a silver tube. The interchange of the NaOH was assumed to be 100% (Winter, Carlton, and Briscoe, *loc. cit.*).

and at temperatures up to 180°. They suggested that interchange could be accounted for by the formation of either a " quasi-molecule " or an anhydride; *e.g.*, for the bisulphate ion the mechanism would be

either

$$H_2OH^{\cdot} + HSO'_4 \rightleftharpoons H_2O + H_2SO_4$$

$$H_2O + H_2SO_4 \rightleftharpoons H_2O{-}SO_2(OH)(OH) \quad \text{(quasi-molecule)}$$

$$B^{\cdot} + H_2O{-}SO_2(OH)(OH) + HA \longrightarrow BH + HO{-}SO_2{-}OH + H_2O + A'$$

(where B$^{\cdot}$ and A$'$ are Brönsted base and acid respectively)

or

$$H_2OH^{\cdot} + HSO'_4 \rightleftharpoons H_2O + H_2SO_4$$
$$H_2SO_4 \rightleftharpoons H_2O + SO_3$$

It should be noted that the latter mechanism is really the same as mechanism (1), above.

From a study of the interchange of potassium hydrogen sulphate, sodium chromate, chromic anhydride, potassium sulphite, and other salts, Mills (*J. Amer. Chem. Soc.*, 1940, **62**, 2833) concluded that salts suffer interchange through anhydride formation or some other reaction. From a theoretical consideration of the mechanism put forward to account for the interchange of potassium chromate (Winter, Carlton, and Briscoe, *loc. cit.*), Mills concluded that this mechanism (involving the formation of the dichromate ion Cr_2O_7'') did not account for the observed rapid interchange, and assumed that this interchange occurs *via* anhydride formation.

The whole problem is complex, and its difficulty is accentuated by the fact that these interchange experiments are necessarily performed in concentrated solutions, about the constitution of which little is known. Some attempt at a mathematical formulation may be made as follows.

Neglect for the moment any consideration of the precise mechanism whereby interchange occurs, and consider the four equations below as representing the net result during the interchange of bisulphates (in the following discussion **O** represents a heavy, and O a normal oxygen atom) :

$$\left.\begin{aligned} SOOOOH' + H\mathbf{O}H &\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} S\mathbf{O}OOOH' + HOH \\ S\mathbf{O}OOOH' + H\mathbf{O}H &\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} S\mathbf{O}OOOH' + H\mathbf{O}H \\ S\mathbf{O}\mathbf{O}OOH' + H\mathbf{O}H &\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} S\mathbf{O}\mathbf{O}OOH' + HOH \\ S\mathbf{O}\mathbf{O}\mathbf{O}OH' \quad H\mathbf{O}H &\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} S\mathbf{O}\mathbf{O}\mathbf{O}\mathbf{O}H' + HOH \end{aligned}\right\} \quad \ldots\ldots\ldots (1)$$

Hence

$$\mathrm{d[H\mathbf{O}H]/d}t = k_1[\mathrm{H\mathbf{O}H}]_t\{[\mathrm{SOOOOH'}]_t + \tfrac{3}{4}[\mathrm{S\mathbf{O}OOOH'}]_t + \tfrac{1}{2}[\mathrm{S\mathbf{OO}OOH'}]_t + \tfrac{1}{4}[\mathrm{S\mathbf{OOO}OH'}]_t\} - k_{-1}[\mathrm{HOH}]_t\{[\mathrm{S\mathbf{OOOO}H'}]_t + \tfrac{3}{4}[\mathrm{S\mathbf{OOO}OH'}]_t + \tfrac{1}{2}[\mathrm{S\mathbf{OO}OOH'}]_t + \tfrac{1}{4}[\mathrm{S\mathbf{O}OOOH'}]_t\} \quad . \quad . \quad . \quad (2)$$

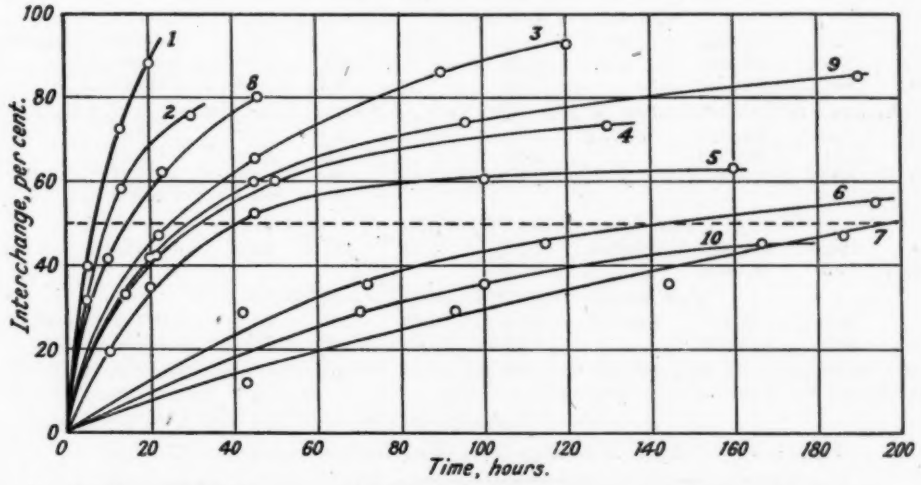
Then if a_t and ε_t be the atom fractions of **O** in the water and the bisulphate respectively at the same time

$$a_t = [\mathrm{H\mathbf{O}H}]_t/[\mathrm{H_2O}], \quad 1 - a_t = [\mathrm{HOH}]_t/[\mathrm{H_2O}]$$
$$\varepsilon_t = \{[\mathrm{S\mathbf{OOOO}H'}]_t + \tfrac{1}{4}[\mathrm{S\mathbf{OOO}OH'}]_t + \tfrac{1}{2}[\mathrm{S\mathbf{OO}OOH'}]_t + \tfrac{1}{4}[\mathrm{S\mathbf{O}OOOH'}]_t\}/[\mathrm{HSO_4'}] \quad . \quad . \quad . \quad . \quad (3)$$

with a similar expression for $1 - \varepsilon_t$. ($[\mathrm{H_2O}]$ and $[\mathrm{HSO_4'}]$ here represent the total amount of water and of bisulphate radical respectively present in the system.)

FIG. 1.

Rates of interchange.



1. $KHSO_4$, 6·13M, 108°. 2. $KHSO_4$, 3·85M, 108°. 3. $KHSO_4$, 6·13M, 100°.
4. $KHSO_4$, 4·53M, 100°. 5. $KHSO_4$, 3·85M, 100°. 6. $KHSO_4$, 2·45M, 100°.
7. $KHSO_4$, 1·226M, 100°. 8. $NaHSO_4$, 6·13M, 100°. 9. $NaHSO_4$, 3·85M, 100°.
10. KH_2PO_4, 2·78M, 100°.

Assuming that $k_1 = k_{-1}$, as will be approximately true, it follows from (2) and (3) that

$$-\mathrm{d}a_t/\mathrm{d}t = k_1[\mathrm{HSO_4'}](a_t - \varepsilon_t) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Now at equilibrium,

$$a_\infty\{[\mathrm{H_2O}] + [\mathrm{HSO_4'}]\} = a_t[\mathrm{H_2O}] + \varepsilon_t[\mathrm{HSO_4'}] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

hence

$$-\mathrm{d}a_t/\mathrm{d}t = k_1(c_1 + c_2)(a_t - a_\infty) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where

$$c_1 = [\mathrm{H_2O}] \text{ and } c_2 = [\mathrm{HSO_4'}]$$

Integrating, we have

$$-\log_e(a_t - a_\infty) = k_1(c_1 + c_2)t + A \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The value of A is found from the limiting conditions: $t = 0$, $a_t = a_0$; so that finally we may write

$$\log_{10}(a_0 - a_\infty)/(a_t - a_\infty) = k(c_1 + c_2)t \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Equation (8) has been applied to the experimental data and the results are given in Table III.

In all cases k has been calculated with t in hours and the concentrations c_2 and c_1 (= 55·56) in g.-mols./l. These results are presented in Fig. 2, the values of k for the interchange of potassium chromate being multiplied by 10^{-3} to bring them to a convenient magnitude.

On examining the results of the bisulphate interchange, it is seen that this approach does not give a constant value for k, neither is k, as so calculated, independent of the concentration of bisulphate. It is possible to show that the stoicheiometric concentration of bisulphate may not be the only concentration term necessary.

Titani and Goto (*loc. cit.*) have suggested that the interchange may occur through the formation of sulphuric acid from bisulphate ions, followed by interchange through the medium of a " quasi " molecule $H_2O{-}SO_2(OH)(OH)$

In view of the observed rapid interchange of sulphuric acid, and of the non-interchange of sodium sulphate in neutral or alkaline solution, this suggestion would appear quite reasonable. We have then

$$H^+ + HSO_4' \rightleftharpoons H_2SO_4$$

TABLE III.

Interchange of $KHSO_4$ *at* 100° ($a_0 = 0{\cdot}01167$).

c_2.	t (hrs.).	Interch., %.	a_t.	a_∞.	$k \times 10^4$.	c_2.	t (hrs.).	Interch., %.	a_t.	a_∞.	$k \times 10^4$.
6·13	22	47·0	0·01000	0·00811	2·02	3·85	100	60·1	0·01011	0·00911	1·18
,,	45	65·6	0·00933	,,	1·67	,,	160	63·0	0·01006	,,	0·76
,,	90	86·0	0·00861	,,	1·52	2·45	42	29·0	0·01117	0·00994	6·08
,,	120	92·2	0·00839	,,	1·54	,,	72	35·5	0·01106	,,	4·52
4·53	14	32·7	0·0107	0·00878	2·11	,,	115	45·1	0·01089	,,	3·90
,,	22	42·3	0·0101	,,	1·45	,,	194	55·0	0·01072	,,	3·07
,,	50	60·0	0·00995	,,	1·31	1·226	43	11·8	0·01156	0·01073	0·221
,,	136	73·0	0·00956	,,	0·70	,,	93	29·4	0·01142	,,	0·254
3·85	10	19·6	0·01117	0·00911	6·48	,,	144	35·3	0·01134	,,	0·230
,,	20	34·8	0·01078	,,	4·02	,,	186	47·1	0·01123	,,	0·260
,,	45	52·2	0·01033	,,	2·29						

Interchange of $KHSO_4$ *at* 108° ($a_0 = 0{\cdot}01033$).

6·13	5	40·0	0·00906	0·00711	7·07	3·85	5	31·7	0·00961	0·00806	5·58
,,	13	72·4	0·00800	,,	6·97	,,	13	58·5	0·00900	,,	4·96
,,	20	88·0	0·00750	,,	7·43	,,	30	75·6	0·00861	,,	3·45

Interchange of $NaHSO_4$ *at* 100° ($a_0 = 0{\cdot}01033$ for $c_2 = 6{\cdot}13$; $a_0 = 0{\cdot}01167$ for $c_2 = 3{\cdot}85$).

6·13	10	41·4	0·00900	0·00711	3·76	3·85	20	41·3	0·01061	0·00911	1·95
,,	23	62·0	0·00833	,,	2·97	,,	45	60·1	0·01011	,,	1·53
,,	46	80·0	0·00772	,,	2·54	,,	96	74·0	0·00977	,,	1·03
						,,	190	84·8	0·00950	,,	0·70

Interchange of KH_2PO_4 *at* 100° ($a_0 = 0{\cdot}00867$).

2·78	70	29·0	0·00817	0·00694	0·363	2·78	167	45·0	0·00789	0·00694	0·267
,,	100	35·5	0·00806	,,	0·324						

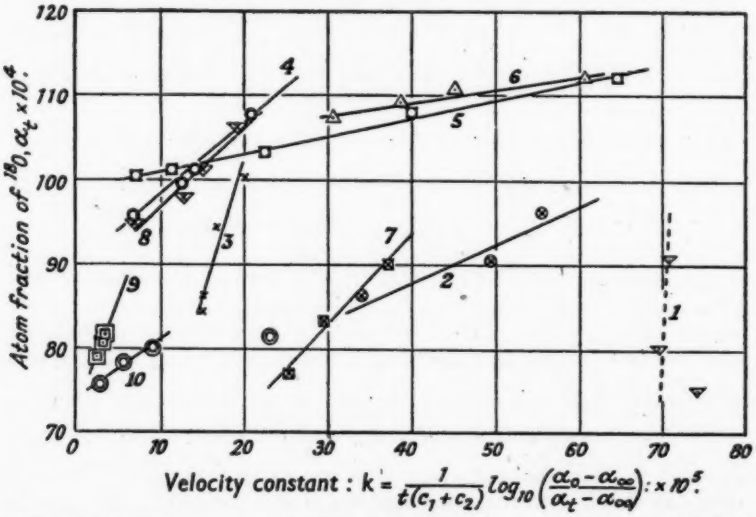
Interchange of K_2CrO_4 *at* 20° ($a_0 = 0{\cdot}00833$).*

1·66	0·5	23·5	0·00811	0·00739	23·3 †	1·66	5·5	52·9	0·00783	0·00739	5·95 †
,,	2·0	35·3	0·00800	,,	9·45 †	,,	24·0	82·4	0·00756	,,	3·14 †

* These results are taken from the previous communication (Winter, Carlton, and Briscoe, *loc. cit.*).
† This value of $k = \log_{10}(a_0 - a_\infty)/(a_t - a_\infty)$.

FIG. 2.

Variation of velocity of interchange (k) *with residual concentration of* $H_2{}^{18}O(a_t)$.



1. $KHSO_4$, 6·13M, 108°.
2. $KHSO_4$, 3·85M, 108°.
3. $KHSO_4$, 6·13M, 100°.
4. $KHSO_4$, 4·53M, 100°.
5. $KHSO_4$, 3·85M, 100°.
6. $KHSO_4$, 2·45M, 100°.
7. $NaHSO_4$, 6·13M, 100°.
8. $NaHSO_4$, 3·85M, 100°.
9. KH_2PO_4, 2·78M, 100°.
10. K_2CrO_4, 1·66M, 20°.

If x is the concentration of H^+, $c_2 - x$ that of HSO_4', and ϕ that of H_2SO_4, we have $\phi = (x)(c_2 - x)/K_{H_2SO_4}$, where x is a function of c_2, being approximately determined by the dissociation of HSO_4' into H^+ and SO_4''. It would appear reasonable to assume that the rate-determining step in the interchange would here be the formation and destruction of the " quasi-molecule " $H_2O \ldots H_2SO_4$, in which case the simple relationship given in equation (8) should become :

$$\log_{10}(a_0 - a_\infty)/(a_t - a_\infty) = k_0 t(x)(c_2 - x)(c_1 + c_2)/(c_2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where

$$k_0 = k/K_{H_2SO_4}$$

This may well give a truer picture of the underlying relationships than equation (8), but does not account in any way for the fact that k is not constant over the range of observations at any one concentration. It appears that k varies regularly in the main with the residual heaviness of the water, a_t; why this should be so is obscure, but the dependence is clearly shown in Fig. 2, where a_t is plotted against k. It is seen that within the limits of experimental error, with the exception of the interchange of 6·13M-potassium hydrogen sulphate at 108° (and of 1·226M-potassium hydrogen sulphate at 100°, which is not shown in Fig. 2) the points all lie on straight lines.

Equation (8) has been applied to the observations of the interchange of potassium dihydrogen orthophosphate at 100° and potassium chromate at 20°, with similar results. The apparent large deviation of the first point in the chromate observations is within the limits of error of the density determination ($\pm 1{\cdot}5\gamma d$) and of the time of interchange (approximately ± 10 mins.). The inclusion in this discussion of the observations on potassium chromate interchange seems legitimate, for if the interchange occurs through the reaction $Cr_2O_7'' + H_2O = 2HCrO_4'$, the mathematical investigation leads to an equation of the same form as (9) above (Mills, *loc. cit.*), and it seems reasonable to suppose that the course of the phosphate interchange will closely resemble that of the bisulphate.

It has been suggested by Mills (*loc. cit.*) and by Titani and Goto (*loc. cit.*) that interchange in concentrated solutions may occur through anhydride formation. This conception is difficult to prove directly, as it is not easy to estimate the amount (if any) of anhydride present in any given solution of, say, potassium hydrogen sulphate or potassium chromate. The following mathematical investigation is possible, based on the method used by Mills and Urey (*loc. cit.*) for the system CO_2–H_2O–H_2CO_3–Na_2CO_3. The case of bisulphate interchange will be discussed, the anhydride in this case being assumed to be SO_3. The equilibria possible are :

$$\left.\begin{aligned} SOOO + HOH &\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HHSOOOO \rightleftharpoons H^{\cdot} + SOOOOH' \\ SOOO + H\mathbf{O}H &\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HHS\mathbf{O}OOO \rightleftharpoons H + S\mathbf{O}OOOH' \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

and so on, the equations being analogous to those of (1) above.

Let a_t, β_t, and ε_t represent respectively the atom fraction of **O** at the time t in the water, the anhydride, and the sulphuric acid. Then from (10) we may obtain similar expressions to (2) above for da_t/dt, $d\beta_t/dt$, and $d\varepsilon_t/dt$. From these we arrive finally at the following equations :

$$da/dt = p(\epsilon - a),\ d\beta/dt = q(\beta - \epsilon),\ d\epsilon/dt = r(4\epsilon - 3\beta - a)/4 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

where

$$p = k_1[SO_3],\ q = k_1[H_2O],\ r = k_1[H_2O][SO_3]/[H_2SO_4] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Here also the quantities in square brackets represent the total concentration of anhydride, water, and sulphuric acid present in the reacting system. The solution of equations (11) will be of the form

$$\left.\begin{aligned} a &= a_1e^{-\lambda_1 t} + a_2e^{-\lambda_2 t} \\ \beta &= b_1e^{-\lambda_1 t} + b_2e^{-\lambda_2 t} \\ \epsilon &= c_1e^{-\lambda_1 t} + c_2e^{-\lambda_2 t} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

where

$$\lambda_{1,2} = \tfrac{1}{2}(p - q - r \pm \sqrt{p^2 + q^2 + r^2 + 2pq + pr + qr}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

The boundary conditions are $t = 0$, $\beta = \varepsilon = 0$, $a = a_0$; $t = \infty$, $a = \beta = \varepsilon = a_\infty$.

It will be shown that the mechanism examined above is most likely to be the correct one, but owing to the fact that values of $[SO_3]$ and $[H_2SO_4]$ in solutions of bisulphates of the concentration used in these experiments do not appear to have been determined, it is not possible directly to justify this conclusion, although it is difficult to imagine any other mechanism than the two examined above whereby interchange could occur.

Equation (11) is similar to equation (4) obtained during the simpler analysis, since, because the reaction $H_2SO_4 \rightleftharpoons H^{\cdot} + HSO_4'$ is rapid, ε_t will be a measure of the heaviness of the bisulphate. We have shown in Table III that the simple relationship obtained in (4) does not hold, and the analysis of the interchange which would occur if formation of the anhydride SO_3 is an essential part of the mechanism shows clearly that this will be the case, as equation (4) does not sufficiently define the relationship of ε_t to a_t.

It is possible that the interchange of potassium dihydrogen orthophosphate, and, in view of the calculations of Mills (*loc. cit.*), that of potassium chromate also, may occur through the formation of anhydride. This view is to some extent strengthened by the fact that for these salts also, equation (4) does not represent the state of affairs during interchange (Table III).

It is evident that the observed large retarding action of sodium hydroxide when added to solutions of potassium chromate may very well be accounted for by this new mechanism, since such an addition would largely suppress the formation of anhydride. It may be that the slower mechanism which occurs in such alkaline solutions (observed at 100°; Winter, Carlton, and Briscoe, *loc. cit.*) involves the ionic mechanism originally proposed. If these interchanges are to be explained on the basis of anhydride formation, the amount of anhydride present in these solutions, except in the case of potassium chromate, must be very small, as the interchange of bisulphates and orthophosphates is relatively slow. The far smaller concentration of anhydride which would appear to be present in the last two cases may be correlated with the greater avidity for water of sulphuric and phosphoric acids.

Some support is given to the anhydride-interchange concept by the following consideration. From equation (13) we have

$$\log_e a_t = -t\{\lambda_1 \log_e a_1 + \lambda_2 \log_e a_2\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

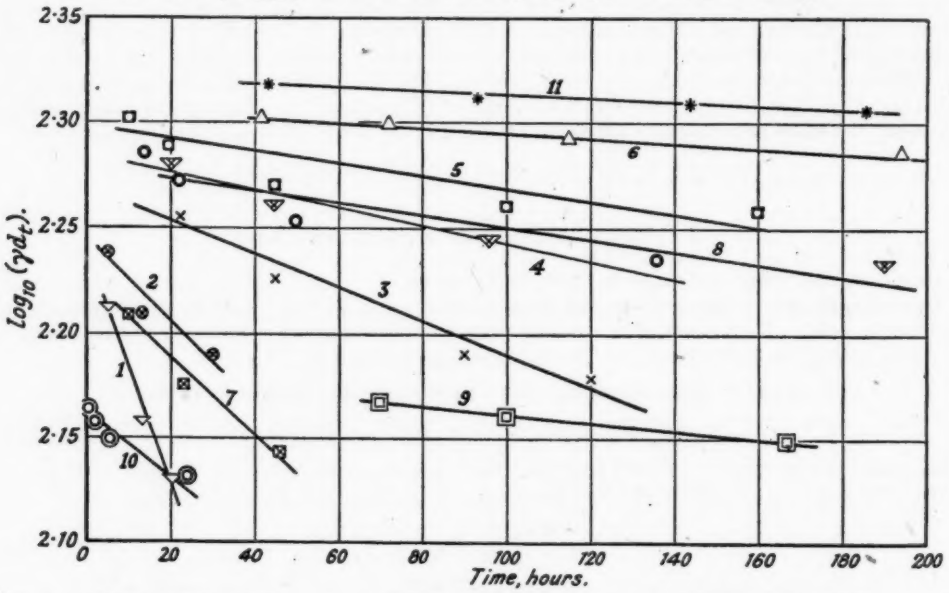
so that if $\log_e a_t$ be plotted against t a straight line should result, the slope of which will be

$$-\{\lambda_1 \log_e a_1 + \lambda_2 \log_e a_2\}.$$

In Fig. 3, $\log_{10}(\gamma d_t)$ has been plotted against t, the values of γd_t being obtained from Table I by subtracting $\Delta\gamma d_t$ from γd_0, and it is seen that the points for each concentration do lie approximately on straight lines, although the agreement in the case of 4·53 and 3·85M-potassium hydrogen sulphate at 100° is not very good, the points here forming a concave curve. The deviations from this generalisation are, however, in most cases within the limits of experimental error. It is obvious from equation (5) that the slope of the lines will not be the same since both λ_1 and λ_2, and a_1 and a_2 are functions of p, q, and r, which themselves are functions of the

FIG. 3.

Variation of $\log_{10}$ *(residual concentration of* $H_2{}^{18}O$*) with time of interchange.*



1. $KHSO_4$, 6·13M, 108°. 2. $KHSO_4$, 3·85M, 108°. 3. $KHSO_4$, 6·13M, 100°.
4. $KHSO_4$, 4·53M, 100°. 5. $KHSO_4$, 3·85M, 100°. 6. $KHSO_4$, 2·45M, 100°.
7. $NaHSO_4$, 6·13M, 100°. 8. $NaHSO_4$, 3·85M, 100°. 9. KH_2PO_4, 2·78M, 100°.
10. K_2CrO_4, 1·66M, 20°. 11. $KHSO_4$, 1·226M, 100°.

concentration of the solution. It is noteworthy also that, not only do the bisulphate–water systems appear to interchange through this mechanism, but also potassium chromate–water and potassium dihydrogen orthophosphate–water. It is necessary to bear in mind the possibility in all these cases of the reversible formation of traces of condensed acids (such as $H_2S_2O_7$, $H_4P_2O_7$, and $H_2Cr_2O_7$) and their salts. Salts of these acids are known, and such reversible reactions, occurring only to a very small extent, might conceivably account for the observations. In this connection, however, the results of experiments 48, 49, and 50 dealing with pyrophosphate interchange are of interest; here it is shown that in neutral, alkaline, or weakly acid solutions of sodium pyrophosphate no large interchange occurs after up to 64 hours' heating at 100°. It therefore seems unlikely that any such reaction as $2HPO_4'' \rightleftharpoons H_2O + P_2O_7''''$ occurs in solutions of potassium dihydrogen orthophosphate (see also Blumenthal and Herbert, *loc. cit.*).

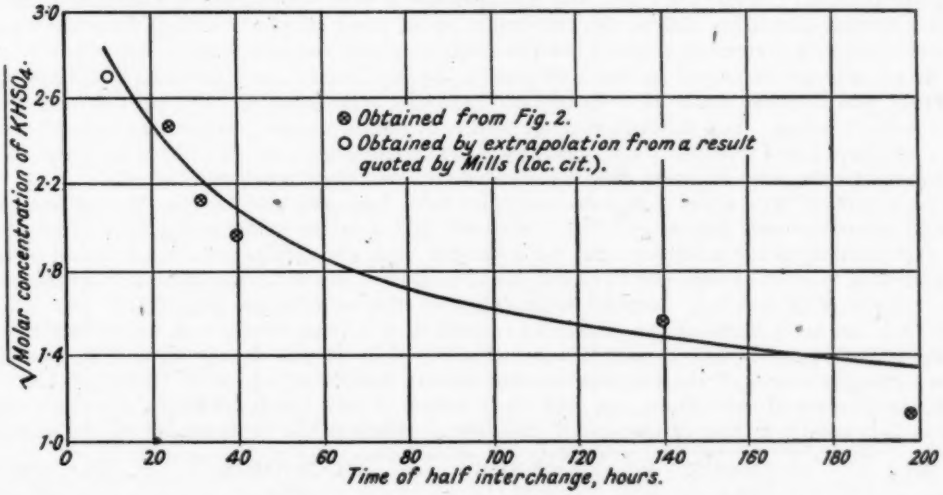
The greater rate of interchange of sodium hydrogen sulphate solutions than of solutions of the potassium salt of the same molarity (see Fig. 1) is difficult to account for with certainty, but is probably attributable to the greater degree of hydration of the sodium ion. This would increase the effective concentration of the bisulphate ion, and so increase the tendency to anhydride formation, giving a more rapid rate of interchange. If this be the true explanation, it throws an interesting light upon the structure of concentrated aqueous solutions: since no appreciable falling off is apparent in the rate of interchange, which proceeds smoothly to approach 100%, it would appear that the forces attracting water molecules to the sodium ions are so much stronger than in the case of the potassium ions as to cause an appreciable increase in $[SO_3]$, but yet are in neither case so strong as to "bind" the water completely and so prevent it from suffering interchange. It may be necessary to exclude from the above generalisation the interchange of 3·85M-potassium hydrogen sulphate at 100°, which does show a falling off in the rate of interchange after interchange has reached 50% (see Fig. 1).

This may be a solution of such a concentration that the two tendencies outlined above are nearly balanced, so that some of the water is more or less completely " bound " to the potassium ions, and so suffers slower interchange than the remainder. In solutions more concentrated than this, the interionic forces may be sufficiently large to ensure a regular exchange of molecules between the cation- and the anion-water, while in less concentrated solutions (where the reaction was not followed above 50% interchange) the fraction of the total water which is bound to the cation may well be so small as to have no detectable effect on the reaction rate until more than 50% interchange has occurred. This theory would mean that in the more dilute solutions the cation water is in fact very rigidly bound, as the number of collisions which would occur between a molecule of cation water and molecules of non-cation water during, say, 100 hrs. at 100° is enormous. It may be noted that Everett and Wynne-Jones (*Trans. Faraday Soc.*, 1939, **35**, 1380) explained the decrease in heat capacity accompanying the ionisation of an acid by assuming that certain rotational degrees of freedom of the solvent molecules around the ions were " frozen out."

The effect of the addition of potassium chloride, hydrochloric acid, sulphuric acid, and sodium perchlorate to solutions of bisulphate is in all cases to increase the rate of interchange above that of the pure bisulphate solution. The acids most probably act by virtue of their hydrogen ions, which would cause an increase in the concentration of undissociated sulphuric acid, and so of the anhydride. The salts would increase the effective concentration of the bisulphate by attracting water of hydration to their constituent ions. On this basis, however, it is not easy to explain the rapid interchange of relatively dilute solutions of sulphuric acid (Expts. Nos. 39 and 40, Table II). In view of the notable avidity of sulphuric acid for water, it is possible that some fundamental change takes place at the moment of mixing, which ensures rapid interchange. In this connection it is of interest that Lichty (*J. Amer. Chem. Soc.*, 1908, **30**, 1834) has shown that pure sulphuric acid dissociates to some extent into water and sulphur trioxide.

FIG. 4.

Effect of concentration upon the time of half interchange for potassium hydrogen sulphate in $H_2{}^{18}O$.



It is noteworthy that acid solutions of sodium perchlorate interchange very slowly at 100°; in this case the interchange can only occur through the free acid, or through an anhydride, since here no condensed acids are known.

Fig. 4 provides independent conformation of the observations of bisulphate interchange quoted in this paper. The square root of the molarity of solutions of potassium hydrogen sulphate has been plotted against the time of half interchange (obtained from Fig. 1). Mills (*loc. cit.*) records a result for interchange of potassium hydrogen sulphate; this result was marked on a replica of Fig. 1, and a curve of the same form as those obtained by us was drawn to pass through this point. The time of half interchange read off from this curve fits into Fig. 4 quite well.

Experimental.—The experimental details are essentially the same as in the previous work (Winter, Carlton, and Briscoe, *loc. cit.*). In expts. 45, 46, and 47 it was assumed that all the hydrochloric acid (liberated from potassium hydrogen sulphate and potassium chloride or present originally as such in the reaction tube) was distilled over with the water during the first distillation. A calculated slight excess of solid sodium hydroxide was added to this distillate, and the distillation repeated. This second distillate was then purified as usual. A correction for the (light) water liberated from the alkali was applied when calculating the results.

Grateful acknowledgment is made of the assistance given to this work by a grant from Messrs. Imperial Chemical Industries, Ltd., also of a Royal Scholarship and a maintenance grant from the Kent Education Committee which has enabled one of us (E. R. S. W.) to take part in the investigation.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, LONDON, S.W.7. [*Received, April 1st.*, 1942.]

133. *The Associating Effect of the Hydrogen Atom. Part XI. Hydrogen Bonds involving the Sulphur Atom. The* S–H–N *Bond.*

By Gordon Hopkins and Louis Hunter.

By an examination of the molecular condition of 35 organic sulphur compounds, it is shown that thioamides possessing the group –NH·CS– are associated by virtue of intermolecular S–H–N bonds. Replacement of the imino-hydrogen atom, or its engagement in chelate ring formation, prevents association by rendering such bonds impossible. The unimolecular state of thiodiphenylamine compared with the high molecular association shown by thioacridone supports the view that only hydrogen capable of tautomeric transfer will take part in S–H–N bonds, and a common cause for both association and tautomeric character is suggested. Derivatives of thioformamide show abnormal association not necessarily dependent on hydrogen bonds.

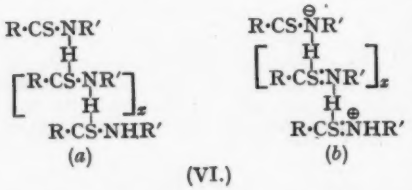
Although there is no lack of evidence that the sulphur atom can donate electrons to form a co-ordinate bond with a great variety of other atoms, it has been generally assumed (see, *inter alia*, Sidgwick, "The Covalent Link," Cornell, 1933, p. 164; Lassettre, *Chem. Reviews*, 1937, **20**, 267; Pauling, "The Nature of the Chemical Bond," Cornell, 1940, p. 290) that it is reluctant to share electrons with the hydrogen atom to form a hydrogen bond. This conclusion has been reached mainly by a consideration of the abnormal physical properties of water when compared with those of hydrogen sulphide, and of the absence of molecular association in thioalcohols and thiophenols (v. Auwers, *Z. physikal. Chem.*, 1899, **30**, 529). Such evidence is obviously only valid against the S–H–S bond.

On the other hand, there are various indications that the sulphur atom can form hydrogen bonds of the type S–H–O and S–H–N possessing considerable stability; *e.g.*, compounds formed between quinones and mercaptans or thiophenols (Beilstein's Handbuch, 4th Edn., Vol. VII, pp. 615, 616, 646) have long been known, whose quinhydrone-like character is strongly suggestive of a S–H–O structure. The molecular association of thioacetic acid (v. Auwers, *loc. cit.*) and the tautomeric behaviour of the thioacids, if attributable to a cause similar to that which prevails in the carboxylic acids, must denote a S–H–O structure in these compounds. Contemporary American workers have recently attributed the anomalous behaviour of mercaptans in certain donor solvents in regard to heats of mixing (Copley, Marvel, and Ginsberg, *J. Amer. Chem. Soc.*, 1939, **61**, 3161), and infra-red absorption (Gordy and Stanford, *ibid.*, 1940, **62**, 497), to the formation of weak S–H–N and S–H–O bonds. It is difficult, without further evidence, to interpret the Raman spectroscopic work of Saunders, Murray, and Cleveland (*ibid.*, 1942, **64**, 1230) on solutions of thiophenol in donor solvents, but it seems clear that some kind of interaction is indicated between thiophenol and dioxan.

In previous parts of this series numerous examples have been given of the parallel between tautomeric character and molecular association, and have indicated that a factor contributing more than any other to hydrogen-bond stability is the condition that the hydrogen atom constituting the bond should be tautomeric. We have, therefore, sought evidence of hydrogen-bond formation in the thioamides and the thioanilides, the tautomeric behaviour of which is formally represented by the equilibrium $R{\cdot}CS{\cdot}NHR' \rightleftharpoons R{\cdot}C(SH){:}NR'$. An examination has been made of the molecular condition of a large number of thioamides by cryoscopic measurement of molecular weight in naphthalene solution. The results clearly show that, provided one or both of the hydrogen atoms of the thioamido-group remain unsubstituted (as in I and II), the compounds exhibit a marked degree of association, but that replacement of both amide-hydrogen atoms by alkyl or aryl groups (as in III) results in loss of associated character. Whether the replacement of the second (imino-)

$R{\cdot}CS{\cdot}NH_2$	$R{\cdot}CS{\cdot}NHR'$	$R{\cdot}CS{\cdot}NRR'$	$CH_3{\cdot}CS{\cdot}NMePh$	$CH_3{\cdot}C(SMe){:}NPh$
(I.)	(II.)	(III.)	(IV.)	(V.)

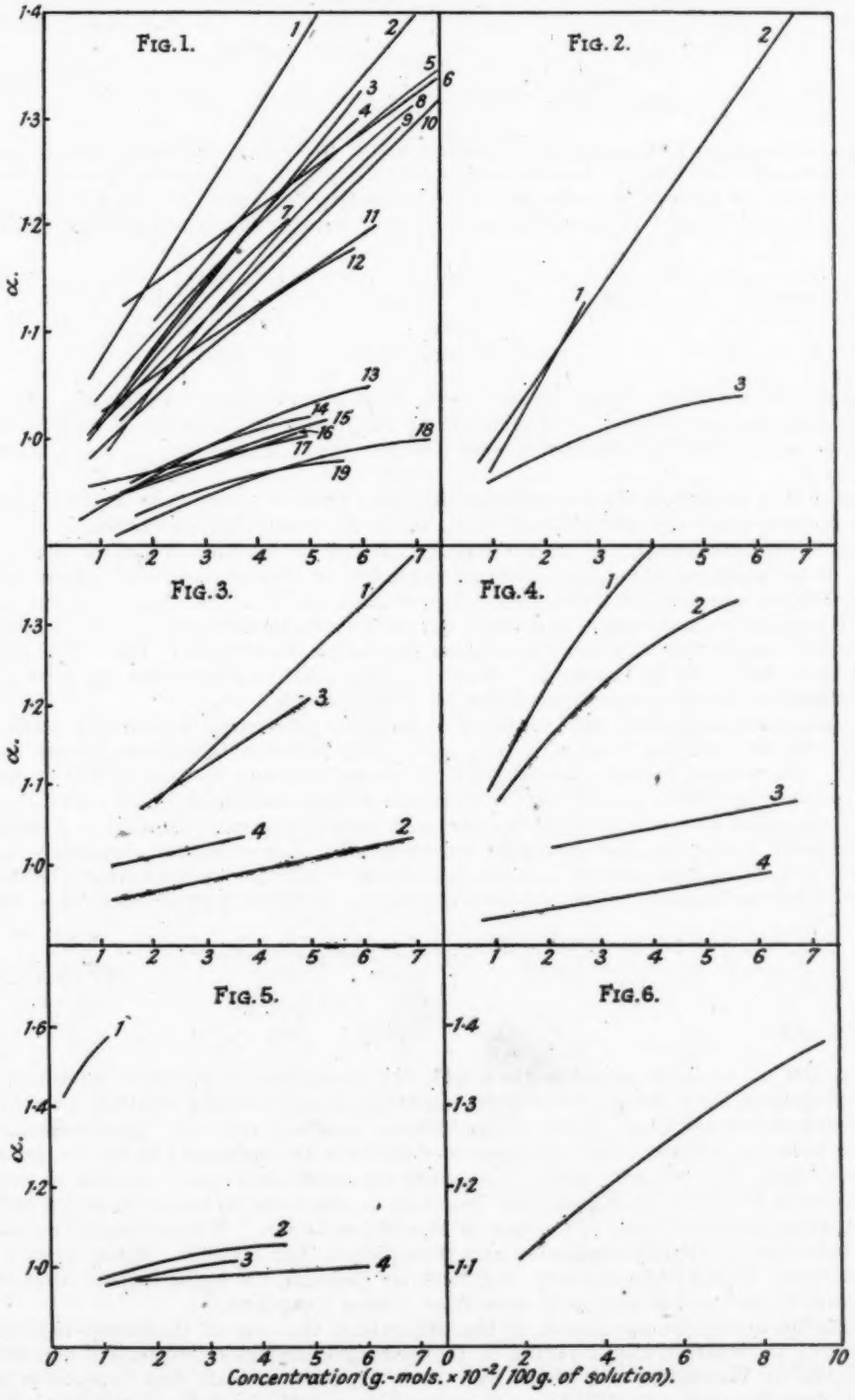
hydrogen atom is effected in the thioanilide (as in IV) or in its mercapto-imide tautomer (as in V), the resulting check in association is the same in both cases. As in previous parts of this series, molecular association is inferred from the molecular weight measurements in all cases where the factor of association (α) rises steeply with increasing concentration: a steep association–concentration curve is taken to indicate molecular association, whereas a flat or gently sloping curve (in the region, $\alpha = 1$) is interpreted as absence of association. Fig. 1 shows that the thioamides fall sharply into two classes, those possessing a free imino-group being highly associated, and those in which the imino-hydrogen atom has been replaced being unimolecular. The suggestion is therefore made that the association of thioamides of the former class is a consequence of intermolecular union through hydrogen bonds, the imino-group of one molecule sharing its hydrogen atom with the sulphur atom of a second, and resulting in polymers united through S–H–N bonds, of a type similar to those previously postulated for amides and sulphonamides (Chaplin and Hunter, J., 1937, 1114). A chain polymer containing $x + 2$ molecules connected by S–H–N bonds is shown in (VI), in which (*a*) and (*b*) are unperturbed structures of the resonance hybrid. Such a polymer will show the properties usually attributed to the tautomeric equilibrium $R{\cdot}CS{\cdot}NHR' \rightleftharpoons R{\cdot}C(SH){:}NR'$.



(VI.)

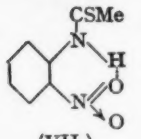
Further confirmation that the imino-hydrogen atom is responsible for the association of thioamides has been obtained by the synthesis of a number of thioanilides in which the anilido-hydrogen atom is engaged

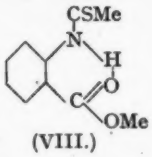
in chelate ring formation with suitably constituted ortho-substituents. Thus, although thioacetanilide (II; R = Me, R′ = Ph) shows a high degree of association, *thioacet-o-nitroanilide* (VII), *methyl thioacetanthranilate* (VIII), and *2-thioacetamido-5 : 4′-dimethylazobenzene* (IX) are all substantially unimolecular (Figs. 2 and 3).

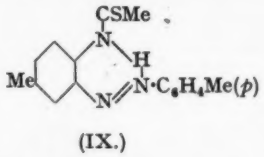


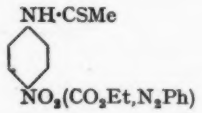
In these compounds it is evident that *intra*-molecular co-ordination of the anilido-hydrogen atom renders it no longer available for *inter*-molecular co-ordination of the type postulated for thioacetanilide. On the other hand, isomers (or close analogues) of these compounds having *m*- or *p*-substituents (*e.g.*, X), in which the donor

groups are too far removed to involve the anilido-hydrogen atom in chelate ring formation, prove to be as highly associated as the parent thioacetanilide (Figs. 2 and 3).

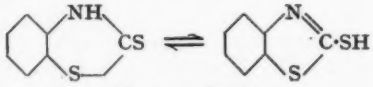

(VII.)

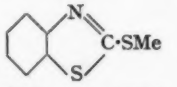

(VIII.)

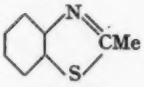

(IX.)

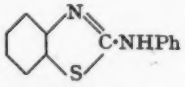

(X.)

Observations have also been extended to thioamides whose $-NH\cdot CS-$ group forms part of a cyclic system. Attention was particularly directed to 1-thiolbenzthiazole (XI) partly on account of its tautomeric character, and partly because of the remarkable reduction (130°) in melting point brought about by its methylation to 1-methylthiobenzthiazole (XII). This contrasting behaviour strongly suggests molecular complexity in the


(XI; m. p. 179°.)


(XII; m. p. 49°.)

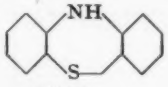

(XIII.)

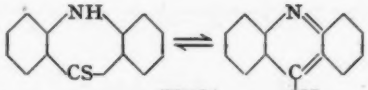

(XIV.)

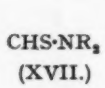
former compound, and molecular weight measurements show it to be highly associated, whereas the latter is substantially unimolecular (Fig. 4). Confirmation of the divergent character of (XI) and (XII) is also indicated in their widely differing dipole moments (Oesper, Lewis, and Smyth, *J. Amer. Chem. Soc.*, 1942, **64**, 1130).

In accordance with expectations, 1-methylbenzthiazole (XIII) is completely unassociated. This compound, though possessing nitrogen and sulphur atoms, has no tautomeric hydrogen atom to provide the bridge necessary for molecular association, and indeed may legitimately be regarded as a cyclic analogue of (V), the *o*-phenylene (or benz) group providing the substituent attached to both nitrogen and sulphur atoms. In this connexion, examination was made of 1-phenylaminobenzthiazole (XIV) in the expectation that it would prove similar to (XIII) in regard to molecular association. Fig. 4 shows, on the contrary, that it is strongly associated, and there seems little doubt that this is due to amidine association (Part VIII, J., 1941, 777), especially as this compound has been shown (R. F. Hunter and Wali, J., 1937, 1513) to possess the character of a semicyclic amidine; it is therefore clearly a case of association by N–H–N bonds.

The belief, previously expressed, that tautomeric character predisposes a hydrogen atom to hydrogen-bond formation, receives striking support from a comparison between thiodiphenylamine (XV) and thioacridone (XVI). The former, though possessing all the atoms necessary to form a S–H–N bond, does not, in fact, do so, as is amply evident from its flat association–concentration curve (Fig. 5, curve 4). On the other hand, thioacridone, which contains sulphur, nitrogen, and hydrogen atoms combined in a manner such that the latter is markedly tautomeric, has properties consistent with high molecular complexity; *e.g.*, it is very sparingly soluble in hydrocarbon solvents, and its high melting point (275°) is very greatly reduced by replacement of its tautomeric hydrogen atom (*e.g.*, *S*-methyl ether, m. p. 114°; *S*-ethyl ether, m. p. 65°; *S*-benzoyl


(XV.)


(XVI.)


(XVII.)

derivative, m. p. 209°). Although insufficiently soluble in hydrocarbons to permit of molecular weight determination in naphthalene, thioacridone shows high association in nitrobenzene solution, whereas its *S*-methyl and *S*-benzoyl derivatives are unassociated (in naphthalene solution) (Fig. 5). Association in nitrobenzene solution may be taken to indicate a marked degree of stability in the associated molecules, for a solvent with such strong donor properties will tend rather to simplify the solute molecules. In view of these facts, thioacridone is considered to have a chain-polymeric structure in which the molecular units are held together by S–H–N bonds formed between CS and NH groups in adjacent molecules. We may legitimately conclude from the divergent behaviour of thiodiphenylamine and thioacridone that bivalent sulphur when a member of a cyclic system does not form hydrogen bonds, and that, for example, the cyclic sulphur atom in 1-thiolbenzthiazole (XI) plays no part in the molecular association of that compound.

In considering the molecular association of the thioamides, the case of thioformyl derivatives deserves particular mention. A review of the properties of thioformamide and its *N*-substituted derivatives, many of which are described by Willstätter and Wirth (*Ber.*, 1909, **42**, 1908), reveals that they are in many respects abnormal. The dialkyl compounds (XVII) are liquids of particularly high boiling point showing many of the characteristics of high molecular complexity. The simplest member, thioformdimethylamide (XVII; R = Me), has been the subject of preliminary study, and proves to be highly associated in benzene solution (Fig. 6). The cause of this association is at present obscure, for there can be no possibility of S–H–N bonds; but it is

noteworthy that the thioformyl group (H·CS·) is structurally identical with the group characteristic of the thioaldehydes, and is well known to be active in causing polymerisation in those compounds. For this reason, molecular-weight data obtained for thioformyl derivatives must be interpreted with caution, and in the present measurements only one such compound (thioformanilide, Fig. 1, curve 6) is included. The study of substituted thioformamides is being continued.

Experimental.

With the two exceptions noted in the following tables, molecular weights were measured cryoscopically in naphthalene. The m. p. of thioacet-*o*-toluidide (66°) confirms that recorded by Wallach (*Ber.*, 1880, **13**, 529) and conflicts with that given (91—92°) by Worrall (*J. Amer. Chem. Soc.*, 1918, **40**, 415).

The following new thioamides were all prepared by the action of phosphorus pentasulphide on the corresponding amide, by heating them either alone or, in better yield, in boiling dry xylene.

Thioacet-m-*toluidide*, buff, crystalline powder, m. p. 64° (Found: S, 19·6. $C_9H_{11}NS$ requires S, 19·4%). *Thiopropion*-p-*toluidide*, fine yellow plates from alcohol, m. p. 52—53° (Found: N, 7·8; S, 18·0. $C_{10}H_{13}NS$ requires N, 7·8; S, 17·9%). *Thioacetethylanilide*, very pale yellow, crystalline powder from alcohol, m. p. 49° (Found: N, 7·7; S, 17·9. $C_{10}H_{13}NS$ requires N, 7·8; S, 17·9%). *Thioacetobenzylanilide*, small, cream-coloured prisms from alcohol (charcoal), m. p. 82—83° (Found: S, 13·2. $C_{15}H_{15}NS$ requires S, 13·3%). *Thiobenzobenzylanilide*, bright lemon-yellow crystalline powder from alcohol (charcoal), m. p. 119—120° (Found: N, 4·5; S, 10·7. $C_{20}H_{17}NS$ requires N, 4·6; S, 10·6%). *Thioacet*-o-*nitroanilide*, orange platelets from acetic acid, m. p. 109° (Found: S, 16·3. $C_8H_8O_2N_2S$ requires S, 16·3%). *Thioacet*-m-*nitroanilide*, sulphur-yellow, crystalline powder from acetic acid, m. p. 98° (Found: S, 16·3%). *Thioacet*-p-*nitroanilide*, fine, sulphur-yellow crystalline powder from acetic acid, m. p. 175° (Found: S, 16·4%). *Methyl thioacetanthranilate*, pale yellow, glistening platelets from acetic acid, m. p. 110—111° (Found: S, 15·2. $C_{10}H_{11}O_2NS$ requires S, 15·3%). *Ethyl* p-*thioacetamidobenzoate*, pale yellow needles from 50% acetic acid, m. p. 98° (Found: S, 14·3. $C_{11}H_{13}O_2NS$ requires S, 14·35%). p-*Thioacetamidoazobenzene*, light red-brown, glistening plates from aqueous acetic acid, m. p. 143—144° (Found: S, 12·7. $C_{14}H_{13}N_3S$ requires S, 12·55%). 2-*Thioacetamido*-5 : 4′-*dimethylazobenzene*, dark brown, crystalline powder from xylene, m. p. 137—139° (Found: S, 11·5. $C_{16}H_{17}N_3S$ requires S, 11·3%).

Molecular-weight Data.—In the following tables, concentrations are expressed as g.-mols. × 10^{-2}/100 g. of solution, the formula weights appearing in parentheses; *M* is the apparent molecular weight deduced according to ideal-solution laws; the association factor (*a*) is calculated as the ratio of *M* to the formula weight.

Fig. 1.

Thioacetamide (75). (Curve 1.)

Concn.	*M.*	*a.*
0·825	79	1·06
1·605	84	1·12
2·90	92	1·22
3·74	97	1·30
4·48	101	1·35
5·38	107	1·42

Thiobenzamide (137). (Curve 2.)

Concn.	*M.*	*a.*
2·03	152	1·11
3·48	164	1·20
5·45	179	1·31
7·06	191	1·40
9·10	208	1·52

Thioacet-*p*-toluidide (165). (Curve 3.)

Concn.	*M.*	*a.*
0·86	165	1·00
2·12	180	1·09
3·60	196	1·19
4·91	208	1·26
6·02	219	1·33

Thioacetanilide (151). (Curve 4.)

Concn.	*M.*	*a.*
1·12	155	1·02
1·97	164	1·08
2·83	172	1·14
3·67	179	1·19
4·53	186	1·23
5·49	194	1·28
5·82	196	1·30

Thioacet-*m*-toluidide (165). (Curve 5.)

Concn.	*M.*	*a.*
0·90	172	1·04
2·58	186	1·13
3·33	193	1·17
4·80	205	1·24
6·25	214	1·30
7·86	226	1·37

Thioformanilide (137). (Curve 6.)

Concn.	*M.*	*a.*
1·44	155	1·13
4·18	166	1·21
5·83	177	1·29
7·51	185	1·35
8·77	192	1·40

Thioacet-*o*-toluidide (165). (Curve 7.)

Concn.	*M.*	*a.*
0·77	165	1·00
1·98	177	1·075
3·24	188	1·14
4·72	199	1·21

Thioacet-α-naphthalide (201). (Curve 8.)

Concn.	*M.*	*a.*
1·15	199	0·99
2·37	218	1·085
3·88	235	1·17
5·45	249	1·24
6·90	265	1·32

Thiopropion-*p*-toluidide (179). (Curve 9.)

Concn.	*M.*	*a.*
0·95	180	1·01
2·08	190	1·06
3·56	204	1·14
5·07	218	1·22
6·71	231	1·29

Thiopropionanilide (165). (Curve 10.)

Concn.	*M.*	*a.*
1·45	169	1·02
2·63	179	1·08
4·20	192	1·16
5·50	201	1·22
7·23	216	1·31
8·66	226	1·37

Thiobenzanilide (213). (Curve 11.)

Concn.	*M.*	*a.*
1·15	219	1·03
1·94	224	1·05
3·60	237	1·11
5·00	247	1·16
6·24	257	1·20

Thiobenz-*p*-toluidide (227). (Curve 12.)

Concn.	*M.*	*a.*
0·87	223	0·98
1·88	236	1·04
3·13	245	1·08
4·38	257	1·13
5·30	262	1·15
5·80	268	1·18

Thioacetodiphenylamine (227). (Curve 13.)

Concn.	*M.*	*a.*
0·62	211	0·93
1·83	216	0·95
2·90	225	0·99
3·96	231	1·02
4·86	233	1·02
5·57	236	1·04
6·10	238	1·05

Thiobenzodiphenylamine (289). (Curve 14.)

Concn.	*M.*	*a.*
1·61	278	0·96
2·50	284	0·985
3·42	286	0·99
4·27	293	1·015
5·00	295	1·02

Thiobenzobenzylanilide (303). (Curve 15.)

Concn.	*M.*	*a.*
1·43	289	0·95
2·55	295	0·97
4·00	302	0·99
5·30	309	1·02

Thioacetmethylanilide (165). (Curve 16.)

Concn.	*M.*	*a.*
0·92	155	0·94
1·72	158	0·96
2·76	160	0·97
3·77	164	0·99
4·37	166	1·01
4·73	166	1·01

Thioacetethylanilide (179). (Curve 17.)

Concn.	*M.*	*a.*
0·80	171	0·96
1·56	172	0·965
2·61	178	0·995
3·33	177	0·99
4·05	178	0·995
4·93	180	1·005

S-Methylthioacetanilide (165). (Curve 18.)

Concn.	*M.*	*a.*
1·32	151	0·91
3·41	157	0·955
4·78	161	0·975
6·15	163	0·99
7·27	165	1·00

Thioacetobenzylanilide (241). (Curve 19.)

Concn.	*M.*	*a.*
1·71	222	0·92
3·15	230	0·96
4·34	234	0·97
5·64	237	0·98

FIG. 2.

Concn.	*M.*	*a.*	Concn.	*M.*	*a.*	Concn.	*M.*	*a.*	Concn.	*M.*	*a.*
Thioacet-*p*-nitroanilide (196). (Curve 1.)			Thioacet-*m*-nitroanilide. (Curve 2.)			Thioacet-*o*-nitroanilide. (Curve 3.)					
0·95	191	0·97	0·67	191	0·98	0·92	188	0·96			
2·11	210	1·07	2·81	220	1·12	2·16	194	0·99			
2·72	220	1·125	4·05	236	1·21	3·47	199	1·015			
			5·61	259	1·32	4·52	202	1·03			
			6·70	274	1·40	5·69	204	1·04			

FIG. 3.

Ethyl *p*-thioacetamidobenzoate (223). (Curve 1.)			Methyl thioacetanthranilate (209). (Curve 2.)			*p*-Thioacetamidoazobenzene (255). (Curve 3.)			2-Thioacetamido-5 : 4′-dimethylazobenzene (283). (Curve 4.)		
2·11	241	1·08	1·22	201	0·955	1·84	272	1·07	1·23	284	1·00
3·42	261	1·17	2·75	203	0·975	2·77	284	1·11	2·50	289	1·02
4·94	282	1·26	4·55	210	1·005	3·42	291	1·14	3·72	293	1·035
6·36	301	1·35	5·77	213	1·015	4·23	300	1·175			
6·98	307	1·38	6·92	216	1·03	4·98	307	1·21			

FIG. 4.

1-Thiolbenzthiazole (167). (Curve 1).			1-Phenylaminobenzthiazole (226). (Curve 2.)			1-Methylthiobenzthiazole (181). (Curve 3.)			1-Methylbenzthiazole (149). (Curve 4.)		
0·92	183	1·095	1·09	244	1·08	2·10	185	1·02	0·75	137	0·92
1·84	202	1·21	2·02	262	1·16	3·69	187	1·035	2·17	141	0·95
2·87	218	1·305	2·92	274	1·215	5·20	192	1·06	3·12	142	0·95
3·78	229	1·375	3·73	285	1·265	6·75	195	1·08	4·08	145	0·97
4·42	237	1·42	4·75	294	1·30				5·05	146	0·98
			5·53	300	1·33				6·31	147	0·99

FIG. 5.

Thioacridone (211). (Curve 1.)			*S*-Methylthioacridone (225). (Curve 2.)			*S*-Benzoylthioacridone (315). (Curve 3.)			Thiodiphenylamine (199). (Curve 4.)		
0·31 *	299	1·42	0·90	219	0·97	1·02	301	0·955	1·61	193	0·97
0·79 *	325	1·54	1·72	225	1·00	2·01	310	0·985	2·64	192	0·97
1·01 *	331	1·57	2·78	230	1·025	2·59	311	0·99	4·00	193	0·97
			3·59	234	1·04	3·54	320	1·015	4·93	195	0·98
			4·46	236	1·05				6·10	198	1·00

FIG. 6.

Thioformdimethylamide (89).

1·92 †	98	1·11	6·09 †	113	1·27	7·96 †	118	1·33	9·66 †	123	1·38
4·12 †	107	1·20									

* Concentrations in nitrobenzene. † Concentrations in benzene.

Grateful acknowledgment is made to the Chemical Society for a grant, and to Imperial Chemical Industries, Ltd., for gifts of chemicals.

UNIVERSITY COLLEGE, LEICESTER. [*Received, July 4th*, 1942.]

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134. *The Crystal Structure of Phosphorus Pentachloride.*

By D. CLARK and H. M. POWELL and (independently) A. F. WELLS.

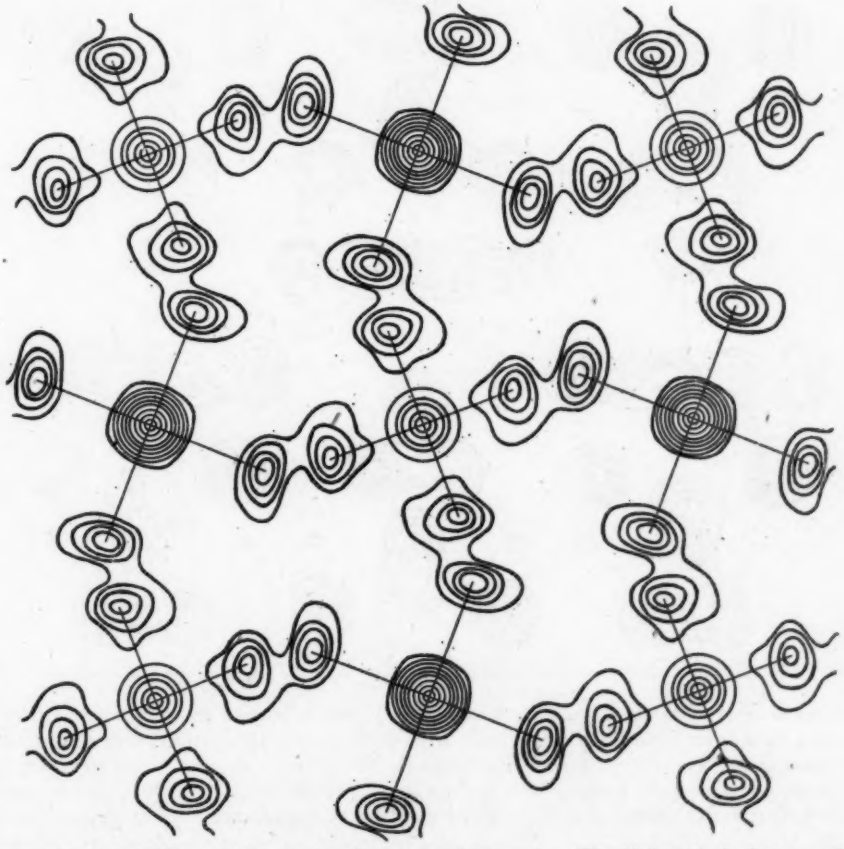
Independent determinations of the crystal structure made from the same photographic data are in good agreement and provide a justification for the use of visually estimated intensities. The tetragonal unit cell contains tetrahedral PCl_4^+ and octahedral PCl_6^- groups.

THERE is proof from electron-diffraction experiments that in the vapour state the molecules of several phosphorus pentahalides have the configuration of a trigonal bipyramid, and the same configuration is found for a number of other molecules of similar formula (Braune and Pinnow, *Z. physikal. Chem.*, 1937, *B*, **35**, 239; Rouault, *Compt. rend.*, 1938, **207**, 620; Moureu, Magat, and Wetroff, *ibid.*, 1937, **205**, 276; Brockway and Beach, *J. Amer. Chem. Soc.*, 1938, **60**, 1836; Ewens and Lister, *Trans. Faraday Soc.*, 1939, **35**, 681; Skinner and Sutton, *ibid.*, 1940, **36**, 668). However, the appreciable electrical conductivity of its solutions (Holroyd, Chadwick, and Mitchell, J., 1925, **127**, 2492) and other observations (Moureu, Magat, and Wetroff, *loc. cit.*, p. 545) suggest that phosphorus pentachloride may be able to exist in an ionised form. The physical properties of the solid lend support to this idea, and a comparison of the Raman spectra in various states shows

that the bipyramidal form of molecules does not persist in the solid (Moureu, Magat, and Wetroff, *loc. cit.*). An *X*-ray investigation has therefore been made in order to determine the structure adopted by the substance in the crystal.

Phosphorus pentachloride crystals are very rapidly decomposed in air owing to the presence of moisture and, for *X*-ray work, must be protected in some way, although Nordenskiold (Groth, " Chemische Kristallographie," I, p. 231), presumably working in a very cold and dry climate, was able to make rough goniometric measurements. Crystals were made in Cambridge by distilling the substance in a vacuum into a small Lindemann glass tube, and Weissenberg photographs of these provided sufficient data for a preliminary determination of the structure. However, the probability of growing good single crystals in this way is small and this method was later abandoned. In Oxford, it was found that single crystals obtained from nitrobenzene solution could be coated with a warm mixture of medicinal paraffin and vaselin which on cooling formed a thin, more or less

FIG. 1.



Fourier synthesis on (001). *Contours at arbitrary equal intervals. The highest peak shows overlapping of* P *and* 2Cl *in* PCl_4 *group.*

solid coating capable, in favourable cases, of preserving the crystal for a few days. Although this experiment failed nine times out of ten, for various reasons, it has the advantage that suitable single crystals may be selected by optical examination.

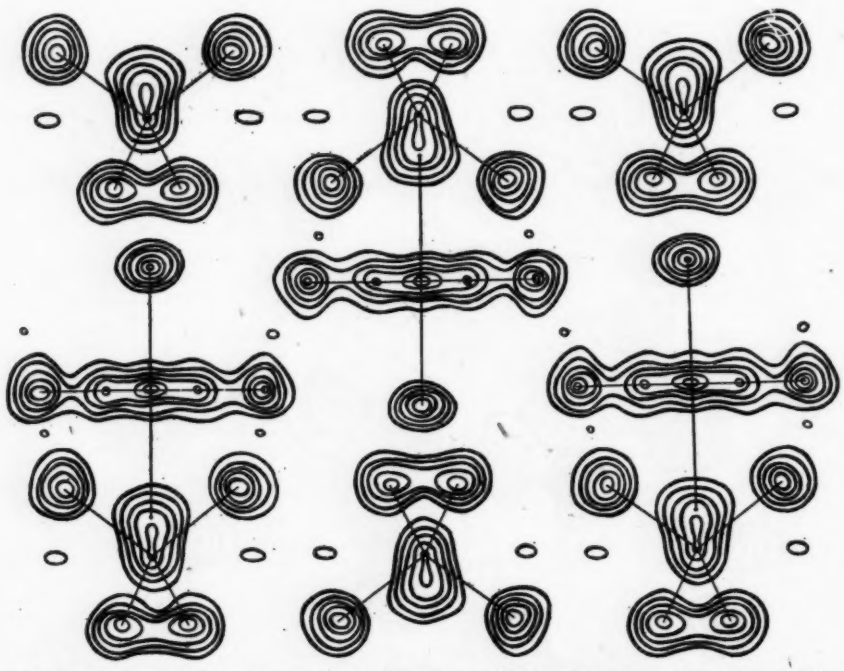
Oscillation photographs obtained from crystals so protected enabled the preliminary structure to be found and were suitable for further detailed work. When it was discovered at this stage that independent investigations in Oxford and Cambridge were taking place, it was decided to complete the experimental work in Oxford and the *X*-ray films were sent after measurement to Cambridge. The structure was then worked out entirely independently in the two laboratories and provides a useful check on the accuracy of the methods employed.

Two series of overlapping 15° oscillation photographs about the [001] and [100] axes were taken with copper radiation. The unit cell dimensions are $a = 9{\cdot}22$, $c = 7{\cdot}44$ A. The density is 2·12 g./c.c., and there are thus four molecules per unit cell. The space-group is shown to be $P4/n$ by the absence of $hk0$ when $h + k$ is odd and the observation that hkl and $\bar{h}kl$ are in general of unequal intensity. Confirmation of the absence of vertical planes of symmetry is provided by the appearance of etch pits on (001) in the form of inverted square pyramids with edges not quite parallel to the edges of the plate.

Among the more likely arrangements of atoms for a compound of empirical formula AX_8 are the following :

(*a*) Discrete molecules AX_6; (*b*) $[AX_4][AX_6]$; (*c*) rings or chains formed by AX_6 octahedra sharing two opposite corners; (*d*) $[AX_4]X$, the AX_4 complex consisting either of discrete tetrahedra or of an extended grouping of AX_6 octahedra sharing four X atoms. Preliminary analysis ruled out all of these possibilities except (*b*), which implies that there are two crystallographically different kinds of phosphorus atom. For convenience, the origin is taken at the centre of symmetry at $\frac{1}{4}\frac{1}{4}0$ as given in the " Internationale Tabellen zur Bestimmung von Kristallstrukturen." The atomic positions are found to be 2P in (*a*) $\frac{1}{4}\frac{1}{4}0,\frac{3}{4}\frac{3}{4}0$; 2P and two different sets of 2Cl in (*c*) $\frac{1}{4}\frac{1}{4}z,\frac{3}{4}\frac{1}{4}\bar{z}$ with their proper values of z; two different sets of 8Cl in general positions (*g*) xyz, $\bar{x}\bar{y}\bar{z}$, etc. This structure contains tetrahedral PCl_4^+ and octahedral PCl_6^- groups, and, by systematic trial, approximate values for all the parameters were found. Signs of F_{hk0} and F_{h0l} were then computed, and the Fourier series for electron density projected on (001) and (010) were evaluated. By successive approximations the final projections, Figs. 1 and 2, were obtained. The independent estimates of parameters given in Table I

FIG. 2.



Fourier synthesis on (100). *Tetrahedral* PCl_4 *and octahedral* PCl_6 *groups shown by ruled lines.*

show very good agreement. As far as we are aware this is the first case in which two entirely independent determinations of a structure have been made from the same photographic data, and it provides an important justification of the use of visually estimated intensities. It must, of course, be remembered that the close agreement of the two sets of parameters does not indicate the possible error in these figures, since any inaccuracies in the experimental data, due, *e.g.*, to absorption of the *X*-rays in the crystal, affect both determinations.

Table II gives calculated F values and two sets of observed F values derived from the independently estimated intensities. The more important interatomic distances are collected in Table III.

TABLE I.

Estimated parameters.

				Oxford.	Camb.					Oxford.	Camb.
$2P_I$	$\frac{1}{4}\frac{1}{4}0$	$\frac{3}{4}\frac{3}{4}0$				$2Cl_I$	$\frac{1}{4}\frac{1}{4}z_2$	$\frac{3}{4}\frac{3}{4}\bar{z}_2$	z_2	$-0{\cdot}09_5$	$-0{\cdot}10$
$2P_{II}$	$\frac{1}{4}\frac{1}{4}z_1$	$\frac{3}{4}\frac{3}{4}\bar{z}_1$	z_1	$-0{\cdot}38$	$-0{\cdot}38$	$2Cl_{II}$	$\frac{1}{4}\frac{1}{4}z_3$	$\frac{3}{4}\frac{3}{4}\bar{z}_3$	z_3	$0{\cdot}34$	$0{\cdot}34$
$8Cl_{III}$	xyz etc.		x	$0{\cdot}31$	$0{\cdot}30_5$	$8Cl_{IV}$	$x'y'z'$ etc.		x'	$0{\cdot}334$	$0{\cdot}337$
			y	$0{\cdot}084$	$0{\cdot}083$				y'	$-0{\cdot}046$	$-0{\cdot}045$
			z	$0{\cdot}15$	$0{\cdot}15$				z'	$-0{\cdot}38$	$-0{\cdot}38$

The PCl_4 and PCl_6 ions are arranged in a structure which is essentially of the cæsium chloride type, but distorted, since these ions are not spherical. Each complex has eight neighbours of the opposite charge. The structure bears some resemblance to that of tetramethylammonium iodide (Wyckoff, *Z. Krist.*, 1928, **67**, 91), but belongs to a lower symmetry class of the tetragonal system; when the negative as well as the positive ions are complex, a more convenient packing is obtained if the vertical planes of symmetry are absent.

The small difference in the phosphorus–chlorine distances in the PCl_6 group may be real but is not significant

TABLE II.

Calculated and observed values of F_{hk0} and F_{h0l}.

F_{hk0} ($hk0$ in order of increasing sin θ).

	Observed.				Observed.				Observed.				Observed.		
$hk0$.	Oxf.	Camb.	Calc.	$hk0$.	Oxf.	Camb.	Calc.	$hk0$.	Oxf.	Camb.	Calc.	$hk0$.	Oxf.	Camb.	Calc.
110	18	18	26	530	17	22	−38	800	18	20	−21	770	20	—	50
200	72	60	−87	350	25	22	−55	820	14	20	−30	860	15	—	−38
220	10	10	21	600	46	52	−43	280	34	34	−60	680	20	—	−26
310	33	32	48	620	88	92	140	660	14	<20	8	1000	22	36	−40
130	76	76	−76	260	27	28	40	750	21	28	−53	950	14	—	16
400	60	56	58	550	24	28	−17	570	24	—	− 9	970	18	—	−27
330	60	54	68	710	12	18	−20	840	12	<20	10	790	9	—	7
420	50	58	−69	170	25	<20	22	480	29	40	50	880	10	—	36
240	44	42	−60	640	20	28	−27	910	28	44	60	1020	24	—	32
510	14	<20	− 9	460	23	28	−55	190	31	44	44	1040	16	—	−30
150	50	58	60	730	14	20	32	930	0	—	7	4100	43	—	−43
440	20	28	42	370	25	<20	−10	390	24	—	−24	1060	6	—	15

F_{h0l} ($h0l$ in order of increasing sin θ)

$h0l$.				$h0l$.				$h0l$.				$h0l$.			
001	0	0	− 7	104	20	14	−11	701	0	0	7	007	0	0	−14
101	30	34	−38	501	43	20	−43	702	84	84	100	107	56	80	57
201	39	40	−32	204	18	26	15	405	0	0	6	506	0	0	4
002	7	<10	−12	403	44	52	57	006	58	28	60	901	0	0	− 7
102	43	44	55	502	19	22	−16	106	46	42	−53	207	0	<20	4
202	10	6	−15	304	21	28	27	206	18	32	−19	902	24	—	17
301	90	72	−66	601	20	26	−24	604	0	0	7	307	20	54	−14
003	15	20	26	503	30	44	−32	505	0	0	11	705	0	—	0
103	62	54	−70	005	69	52	59	801	0	0	11	606	17	—	−18
302	15	16	− 2	404	0	0	− 7	306	17	<20	13	407	39	—	−32
401	0	0	0	602	17	<20	−16	802	0	0	0	903	15	—	−25
203	20	26	−33	205	18	24	−19	406	0	0	3	008	60	56	70
402	24	36	15	305	54	58	63	704	17	—	−24	507	27	25	23
303	0	0	−11	603	0	0	7	605	0	—	10				
004	180	144	−160	504	30	40	28	803	17	—	32				

TABLE III.

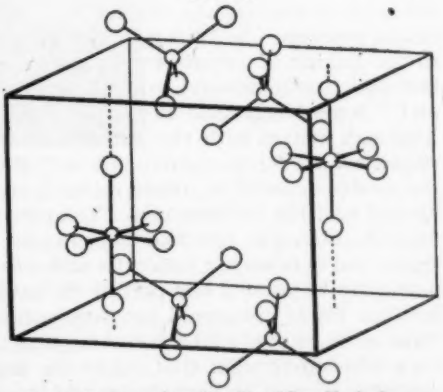
Interatomic distances, A.

	Oxford.	Camb.		
P_I–Cl_{III} in PCl_4	1·97	1·98	Cl_{III}–Cl_{IV}	3·45, 3·6, 3·6, and 3·9
P_{II}–Cl_I in PCl_6	2·08	2·08	Cl_{II}–Cl_{III}	3·43
P_{II}–Cl_{II} in PCl_6	2·08	2·08	Cl_I–Cl_{III}	3·6
P_{II}–Cl_{IV} in PCl_6	2·04	2·05	Cl_{IV}–Cl_{IV}	3·64

Bond angles in PCl_4 tetrahedron: 111° and 119°.

as it is of the same order of magnitude as the possible error. The structure does, however, permit a comparison of the phosphorus–chlorine bond length for two different states of co-ordination of the phosphorus atom in one and the same compound. The decrease in phosphorus–chlorine distance from 2·06 (average) in PCl_6 to 1·98 A. in PCl_4 may be accounted for as follows. The change in covalent radius for a sequence of atoms, in a short period of the periodic table, which use the same orbitals in bond formation is due to the increase of effective nuclear charge in the sequence; it has been shown (Pauling and Sherman, *Z. Krist.*, 1932, **81**, 1) that unit positive charge on an atom of atomic number Z should lead to a decrease of covalent radius of about $\frac{3}{4}$ of the difference between the covalent radii for the atoms of atomic numbers Z and $Z + 1$, owing to the change in screening effect. An opposite effect occurs when the atom has a negative charge. If, in the present case, it is possible to neglect the difference in co-ordination number and the fact that different orbitals are used, a similar argument shows that the difference in bond lengths in PCl_4 and PCl_6 should equal two-thirds of the difference between the single bond radii for silicon and sulphur, the horizontal neighbours of phosphorus in the periodic table, *i.e.*, $\frac{2}{3}$ (1·17 − 1·04) = 0·087 A.; this agrees with the observed difference. Apart from this difference, the P–Cl distance in PCl_4 is itself short by about 0·08 A. of the length 2·05 A. calculated for P–Cl from the sum of the normal tetrahedral covalent radii derived from methyl compounds, with a correction for the charge as above. Similar shortenings are observed for many halogen compounds (see, *e.g.*, Lister and Sutton, *Trans. Faraday Soc.*, 1941, **37**, 393).

FIG. 3.



General view of unit cell: (Small circles—phosphorus; large circles—chlorine.)

LABORATORY OF MINERALOGY AND CRYSTALLOGRAPHY, UNIVERSITY MUSEUM, OXFORD.
CRYSTALLOGRAPHIC LABORATORY, CAMBRIDGE.

[*Received, August 13th*, 1942.]

OBITUARY NOTICE.

HERBERT FREUNDLICH.

1880—1941.

THE death of Professor Herbert Freundlich at Minneapolis, Minnesota, on March 30th, 1941, after an illness (coronary thrombosis) lasting less than a day, deprived the world of science of its most distinguished investigator and expounder of colloid and interfacial phenomena, and a great host of friends in many lands of a man who had won their respect, esteem, and sincere affection.

Herbert Max Finlay Freundlich was born on January 28th, 1880, at Berlin-Charlottenburg, the eldest son of Friedrich Philipp Ernst Freundlich, manufacturer, and Ellen (Nellie), née Finlayson, the daughter of William Finlayson, of Scotland. His father was half-Jewish (his mother being a Jewess), but he was a member of the Christian Protestant Church when he married Miss Finlayson, and all their children were baptised and confirmed in the Protestant Church.

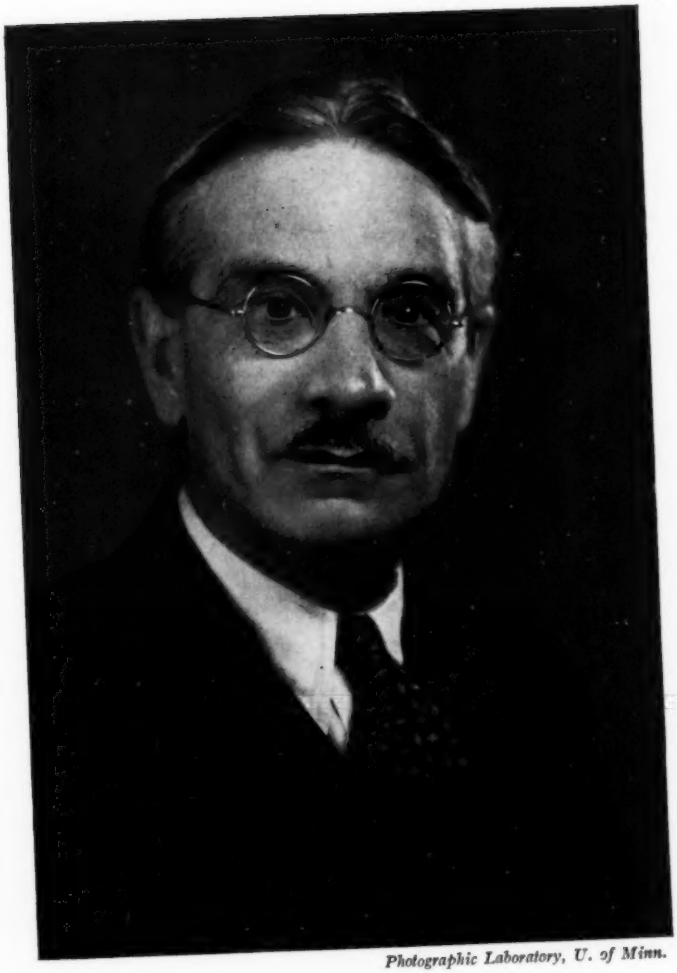
Soon after Herbert's birth, his father, who had been appointed director of an iron foundry at Biebrich-Wiesbaden, bought a house at Biebrich-on-the-Rhine and settled there with his family. So it was in the sunny, light-hearted, and artistic atmosphere of the beautiful Rhineland that Herbert and his brothers and sisters spent a happy childhood and youth.

From his earliest years Herbert Freundlich had a passion for music and musical composition, and for animal study (especially entomology). His brothers and sisters had few dull moments, for under Herbert's energetic leadership something new was always turning up. When they were not singing his songs they were tracking caterpillars under his enthusiastic guidance, or hunting for leaves to feed them with.

After a period of preliminary studies (1886—1892) at the preparatory school and the *Realprogymnasium* at Biebrich, Herbert Freundlich entered the classical side of the " humanistic " Gymnasium (higher secondary school) at Wiesbaden in 1892, successfully completing his studies there with the " certificate of maturity " in 1898. During this period he devoted himself particularly to the study of Greek and German, Greek literature remaining an inspiration which influenced his whole life. Science, however, was to claim the chief allegiance and the lifelong service of this young lover of music and fine literature, and in October, 1898, he entered the University of Munich, where he spent two semesters (one academic year) in preliminary science studies. Deciding on chemistry as his main subject of study and research and attracted, no doubt, by the fame of Wilhelm Ostwald and the rich summer tide of the " new " science of physical chemistry, he moved on to the University of Leipzig. Here he continued his scientific training, studying especially physical chemistry in Ostwald's new physico-chemical Institute in the Linné Strasse, and after four years obtained the Doctorate in February, 1903, with a Dissertation on the " Precipitation (Coagulation) of Colloid Solutions by Electrolytes." It is related that Freundlich was attracted to the study of colloid phenomena by his deep interest in biology, having the intuitive feeling that the investigation of this special branch of physico-chemical science might prove one of the best available approaches to a better understanding of the complex structure and activity of " living " protoplasm. However that may be, it is certainly true to say that throughout Freundlich's life he never lost sight of the intimate relations between colloid and biological science, and took delight on various occasions in drawing the attention of biologists to the current (and relevant) advances in the investigation of colloid systems. In his last years at the University of Minnesota (1938—41) he was devoting special attention to the linking of experimental research in colloid and biological science, as anyone may see who reads his last two (posthumously) printed papers, entitled " Colloid Chemistry of Development and Growth " (1940) and " Some Mechanical Properties of Sols and Gels and their Relation to Protoplasmic Structure " (1942). Although written with the author's customary scientific caution and critical moderation, the reader of these papers cannot fail to observe how well the intuition of the young investigator of 1901—1903 was borne out by the results achieved in colloid research nearly forty years later—results due in large measure to the work of himself and his collaborators. Thixotropic sols and gels, structural viscosity, reversible coagulates, geloids, tactoids, tactosols, intrinsic and morphic double refraction in streaming solutions containing oriented anisotropic and anisometric molecules and micelles—these were indeed phenomena of high importance for him who would try to unravel any part of the nature of protoplasmic structure; and Freundlich was able to point out how the newly discovered and very curious phenomena exhibited by aqueous solutions of the tobacco mosaic virus could be easily interpreted in terms of modern discoveries in colloid science. To the present writer it is a very solacing thought that before his death Freundlich was able to realise this partial though very striking consummation of his early hopes and intuitions.

During the next eight years, *i.e.*, in the period 1903—1911, Freundlich was an Assistant in the Leipzig physico-chemical Institute, holding this position in both the Sections for analytical and physical chemistry; whilst in the period 1904—1906, when Ostwald was having trouble with his opponents in the philosophical Faculty and was travelling abroad a good deal on lecture tours, he carried out the editorial work for the *Zeitschrift für physikalische Chemie*. In October, 1906, he obtained the *venia legendi*, *i.e.*, the status of a Privatdozent or University Lecturer (in both physical and inorganic chemistry) on the basis of a special Thesis (Habilitationsschrift) dealing with " Adsorption in Solutions."

He married in September, 1908, Marie Mann, the daughter of the apothecary Wilhelm Mann at Mainz.



Photographic Laboratory, U. of Minn.

HERBERT FREUNDLICH.

[*To face p.* 646.

She has been described as a lovely fair-haired Rheinländerin, and there is no doubt that Freundlich was deeply attached to her. She bore him two sons and two daughters, but died in 1917 at the birth of her fourth child. This and the death of his second son, from infantile paralysis, were heavy blows from which he never completely recovered.

Although he had relinquished the thought of adopting music as a profession, Freundlich continued the active study and practice of music during his school and university years, becoming a skilled pianist and composing songs, trios, and quartets. An oratorio composed by him was sung at Biebrich-Wiesbaden. Even in later years when he had almost entirely given up piano practice, he could still play Beethoven sonatas, though not from memory (London, 1935).

In 1911 he received a call to the Technische Hochschule at Braunschweig as Associate Professor of Physical Chemistry and Inorganic Technology. He accepted the invitation and went to Braunschweig in the autumn of that year.

During the period 1911—1916 a stream of important researches in colloid science issued from the Braunschweig Laboratory. Here we may note, in passing, the work on electric endosmose with Elissafoff (1912), on swelling-pressure with Posnjak (1912), and the important work on optical phenomena in certain colloid solutions, *i.e.*, stream double refraction, dichroism, and " Schlierenbildung," with the physicist Professor H. Diesselhorst (1915—1916).*

This period of active and fruitful research was interrupted by the war of 1914—18. Owing to general physical weakness Freundlich had not been required to undergo the usual period of military training and had been transferred in 1913 to the *Landsturm*. So he was not called up for active military service in 1914. Being well acquainted with the phenomena of adsorption, he had made, in the autumn of 1915, certain proposals concerning the best use of charcoal in anti-gas respirators. The result was that Professor Haber asked him to come to the Kaiser Wilhelm Institute for Physical Chemistry and Electrochemistry at Berlin-Dahlem to assist in the working out of the best methods of protection against war gases. So Freundlich joined Haber in February, 1916, and did important work in connection with the production, filling, and testing of the materials used in the canisters of the anti-gas outfits. For this good war service he was decorated with a number of military crosses, including the " iron cross with white and black ribbon."

In January, 1919, Freundlich resigned the Braunschweig Professorship, having been invited to become chief of the Division of Colloid Chemistry and Applied Physical Chemistry in Haber's Institute and also an Associate Director of the Institute.

A new career of active research in his chosen field and in one of the most famous centres of research in physical chemistry was now opened to him, and of these great opportunities Freundlich made the fullest use. The work on colloid optics was continued and developed with a number of collaborators, amongst whom the chief was H. Zocher. The theory of the electrokinetic " zeta " potential as distinct from the thermodynamic " epsilon " potential was developed and elaborated (" potential " here means difference of electrical potential) in a number of important papers. The mechanical and rheological properties, such as viscosity and elasticity, of colloid systems were intensively investigated with a number of collaborators. This led to the great series of researches on the phenomenon of thixotropy, rediscovered by Szegvari and Miss Schalek in 1923, and the contrasted phenomenon of dilatancy, discovered many years previously by Osborne Reynolds in England. Special attention was paid to the remarkable optical phenomena due to the presence of non-spherical, *i.e.*, rod-like or plate-like, particles in colloid sols, and Freundlich was able to show how the investigation of such phenomena could lead to valuable conclusions concerning the shape of the particles. As mentioned previously, Freundlich's chief collaborator in this series of researches was H. Zocher, who acted as collaborator also in the beautiful work on the passivity of iron mirrors. Reference must also be made to the discovery of " mechanical " coagulation, and especially to the important researches (with K. Sollner) on the effects produced on gels (especially thixotropic gels) and biological systems by supersonic vibrations. During these years (1919—33) Freundlich created in the Dahlem Laboratory one of the world's chief centres of research in colloid science. In 1923 he was made honorary Professor of Chemistry in the University of Berlin, and the same honour was conferred on him by the Berlin Technische Hochschule in 1930. The University of Minnesota and the Colloid Committee of the National Research Council of the United States invited him in 1925 to be the distinguished guest scholar at the second National Colloid Symposium, held in Minneapolis. Freundlich accepted the invitation and remained in residence at the University during the ensuing summer term, giving a series of lectures on colloid chemistry and captivating his American colleagues and students by his modest and charming personality. On the invitation of the Chemical Society, he delivered the second Liversidge Lecture (London, 1930), the title being " Surface Forces and Chemical Equilibrium."

A dark and tragic shadow was soon to fall on this scene of high and successful endeavour. In the spring of 1933, soon after the rise of the National Socialist Party to power in Germany, Haber and Freundlich were ordered to dismiss all their associates who were not of " pure Aryan race." Rather than do this, they resigned their positions. As is well known, Haber, on the invitation of Sir William Pope, went to Cambridge University in the Autumn of 1933, whilst Freundlich, on the invitation of the writer of this Memoir, came to University College, London, as Honorary Research Associate. Funds were provided for a period of five years by the generosity and wise foresight of the Directors of Imperial Chemical Industries. It may be interesting to mention here that William Rintoul, of Imperial Chemical Industries, and the writer met Freundlich in Germany

* The work with Posnjak and Elissafoff (or some part of it) may have been carried out at Leipzig.

in May, 1933, and conveyed the invitation personally. Freundlich said he would like to bring with him his principal research assistant and collaborator, Dr. Karl Sollner, and this suggestion was readily accepted.

So it came about that in the same College where Thomas Graham had worked Herbert Freundlich came as an honoured and welcome guest to continue his researches. The work on the effects of supersonic vibrations was actively developed with the expert assistance of Dr. Sollner, whilst the researches on thixotropy were extended in many directions and led, for example, to the discovery (with Dr. F. Julius Burger) of the remarkable phenomenon of " rheopexy." It was found, namely, that the time required for the sol $\longrightarrow$ gel transformation of a thixotropic system could be enormously reduced by a gentle rolling or tapping motion of the containing test-tube. It was suggested that this remarkable " rheopectic " effect might be due to an " orthokinetic " acceleration of the formation of the reversible coagulates (geloids), assisted perhaps by orientation due to the presence of highly anisometric particles.

The work on the behaviour of systems containing relatively coarse particles was further extended during the London period, as examples of which may be quoted the interesting papers on quicksand as a thixotropic system, the plasticity of powdered Solnhofen slate and the thixotropic behaviour of its suspensions (with F. Julius Burger), and the sedimentation volume, dilatancy, thixotropic and plastic properties of concentrated suspensions (with A. D. Jones). Reference may also be made to the investigation of the isoelectric point and swelling-pressure of isinglass (with P. S. Gordon), and the thixotropic behaviour of silica gels (with D. W. Gillings).

Although free from any regular courses of lectures, Freundlich gave a number of inspiring special lectures on colloid science to postgraduate workers in the laboratory, and was invited by various outside scientific and technical societies to give discourses on special topics. Everywhere his wide knowledge and learning, his lively and imaginative perception of the possibilities of explanation, application, and further research, and his lucid and cautiously critical exposition of scientific results were highly appreciated by his audiences, and were of the greatest value for the progress of colloid science in Great Britain.

In 1936 the University of Utrecht conferred on him the honorary degree of Doctor of Philosophy. An invitation to be the distinguished guest scholar at the fourteenth National Colloid Symposium, held at the University of Minnesota, came in 1937, and again Freundlich remained (as in 1925) at the University for a series of lectures in the following summer session.

These two successful visits to the United States were very fortunate, since efforts by his English friends to secure a permanent University position for Freundlich in London were, alas, unsuccessful. However, by this time he had many active friends and admirers in the University of Minnesota. The result was that in January, 1938, he was called to that University as Distinguished Service Professor of Colloid Chemistry in the graduate school, without College or Departmental assignment. During the short period that he held this unique position he was very successful in initiating and guiding the researches of advanced students from a variety of fields, such as physiological chemistry, biochemistry, and physical chemistry. How much his services as teacher, investigator, and wise counsellor were appreciated can be seen from the excellent obituary memoir by Professor Ross Aiken Gortner and Dr. Karl Sollner, published in the American Journal *Science* (vol. **93**, pp. 414—416, 1941).

Freundlich was elected a Foreign Member of the Royal Society in 1939, and an Honorary Fellow of the Chemical Society in February, 1938.

In 1923 he married Hella Gellert, who came with him to London in 1933 and accompanied him to America in 1938. Of his two daughters by his first marriage, Kate now lives at Rochester, Minnesota, and Marie married a Dutchman and lives in Holland. His son, Herbert, a radio research physicist, resides at Cambridge, England. Two sisters of Freundlich live in Great Britain. One, Mrs. Elizabeth F. Wardale, has lived most of her life at St. Andrews. Another sister came with Freundlich to England in 1933 and now resides in this country. His brother, the famous astronomer E. Finlay-Freundlich, who was the first astronomer to give important and practical support to Einstein and his theories, is now Professor of Astronomy at the University of St. Andrews.

The results of the scientific researches of Freundlich and his collaborators are contained in more than 200 published papers. When in 1901 he began his first work on the coagulation of " hydrophobic " colloid sols by electrolytes, the results obtained by Linder and Picton, Schulze, and Hardy were known, especially the Schulze–Hardy rules concerning the opposite sign of the electric charge and the valency of the effective ions. Freundlich's work helped greatly in establishing and extending these results, and showed, for example, that the strikingly increased effectiveness of bi- and ter-valent metal ions in coagulating negatively charged sols could not be explained by increasing degrees of hydrolysis of the corresponding salts. It was also shown that many organic ions had a much greater coagulating effect than would be expected from their valency, a result which was also true in many cases for the hydrogen and hydroxyl ions.

His investigations on adsorption in solutions, for example, the adsorption of non-electrolytes and weak electrolytes by charcoal in aqueous and non-aqueous solutions, greatly advanced the knowledge of what was then a somewhat mysterious phenomenon. Although the work of Ostwald and others had established the existence of well-defined reversible equilibria in such cases, Freundlich's work showed the insufficiency of the earlier crude ideas relating to the formation of chemical compounds or solid solutions as explanations of such adsorption phenomena. In this his famous " adsorption-isotherm " played a notable part, and although this equation was of a purely empirical character, was not new, and did not explain the saturation effect, in Freundlich's hands it was of great value in correlating a great mass of experimental material, in giving precision to the

reversible equilibria, and in explaining the relatively great effect in the case of small concentrations of the adsorbed substance.

Freundlich was led to see in adsorption an exemplification of Gibbs' thermodynamic equation relating the excess " surface " amount (per unit interface) of a dissolved solute with the rate of decrease of the surface tension between two fluid phases with increase in bulk concentration of the " adsorbed " solute. Although a surface concentration of this type was shown later by other investigators to be in certain cases in approximate agreement with Gibbs' equation (in its approximate form), it was not possible for Freundlich to deal in this manner with adsorption phenomena where the adsorbent was a solid substance. As is now well known, the work of Haber and especially that of Langmuir has established in such cases a satisfactory theory on the basis of reversible kinetic equilibria and " residual " chemical valencies at the surface of the solid adsorbent.

Freundlich obtained valuable and fruitful results when he applied the concept of adsorption to the explanation of the coagulating effects of ions. The greater effect of organic ions (in comparison with their valency) could now be correlated with a greater " specific " adsorption of such ions. The " taking up " or co-precipitation of the effective ions by the coagulated flocks (a phenomenon already observed and stressed by Picton and Linder) was found to agree with the adsorption formula. Of great importance was Freundlich's explanation of the extraordinarily great and hitherto unexplainable influence of the valency of the effective ions. It was found that the adsorption curves for ions of different valency, for example, those of the " light " metals, were approximately coincident when the concentrations and the adsorbed amounts were reckoned in mols. Since, for coagulation, *equivalent* amounts of ions must be adsorbed (equal amounts of electricity for neutralisation of the electric charges of the colloid particles), the shape of the adsorption curves showed that the necessary concentrations of ions of different valency must lie as widely apart as experiment had shown to be the case.

The marked parallelism between the influence of electrolytes on coagulation and on electrokinetic phenomena (electric endosmose, cataphoresis) led Freundlich to undertake investigations of the latter. Although the physical theory of the " electrical double layer " had been established by Helmholtz, little was known about the effect of electrolytes thereon, and clear ideas were lacking concerning the relationship (or even identity) of the Helmholtzian (electrical) " potential jump " with the " thermodynamic " potential jump introduced by Nernst in his theory of galvanic cells. Freundlich came to the conclusion that the two types of potential difference were essentially different, the electrokinetic one, the " zeta potential ", lying entirely in the liquid phase and being strongly influenced by adsorbed ions. In an experimental investigation with Rona he was able to establish this view by simultaneous measurements of the electrokinetic zeta potential and the thermodynamic " epsilon potential " (so-called Nernst potential) at the same interface. Freundlich's work in this field may indeed be regarded as one of his most important contributions to the science of colloid and interfacial phenomena.

In connection with the subject of adsorption, a brief reference may be made to several interesting investigations, for example, the effect of adsorption on the velocity of crystallisation (a subject also investigated by Marc and Ritzel); the effect of adsorption on certain chemical reactions and their kinetics (the effect of charcoal in acclerating the oxidation of phenylthiourea, of colloidal sulphur in accelerating the transformation of maleic into fumaric acid, and the effect of adsorption on charcoal in *reversing* the normal change of bromoethylamine into dimethylene-imino-bromohydrate); and the velocity of decrease of adsorption in the change of mercuric sulphide from the amorphous to a more crystalline form, and its analogy with the velocity of coagulation.

The work of Zsigmondy had demonstrated the influence of various hydrophilic colloids, such as albumen, gelatin, gum, etc., in protecting hydrophobic sols from coagulation by electrolytes in concentrations otherwise effective. Freundlich made the remarkable discovery that a number of these " protective " colloids when present in very small concentration could produce the opposite effect, that is to say, they could actually promote the coagulating effect of the electrolytes. This phenomenon he termed " sensitisation." It is probable that both the protecting and the sensitising action are related to adsorption and to the isoelectric points of the hydrophilic colloids.

It is well known that gels under suitable conditions can take up a liquid dispersion medium and swell, and that such a swelling can often produce very considerable pressures. This phenomenon had been investigated by Reinke in the case of discs cut from the leaves of *Laminaria*, but it was left to Freundlich to find that well-defined thermodynamically reversible equilibria occur in such cases. His careful quantitative work with Posnjak on the " swelling-pressure " of rubber in organic liquids and of gelatin in water showed that this pressure increased with a high power of the concentration of the gel, and could be thermodynamically related to the vapour pressure of the gel in the same manner as the osmotic pressure of a solution to its vapour pressure. Katz, who soon afterwards carried out an extensive investigation of the vapour pressure and heat of swelling of gels, was able to make considerable use of the relations established by Freundlich.

The chance observation that an " aged " sol of vanadium pentoxide on stirring showed curious effects—optical " streakiness " (Schlieren), " twinkling," and a marked dichroism and birefringence—led Freundlich to a famous series of researches and the creation of a practically new branch of " colloid optics." He was able to show that an enforced optical anistropy, in the form of double refraction and dichroism, could be produced by laminar streaming in sols containing rod-like or plate-like particles. The streaming or laminar flow had the effect of producing a more or less parallel orientation of the elongated highly " anisometric " particles, the degree of orientation depending mainly on the range and intensity of their Brownian motion. Thus a

tube, with a rectangular cross section, full of a non-turbulent streaming liquid containing very small uniaxal crystals with their long axes parallel to the lines of flow will behave like a plate cut from a uniaxal crystal parallel to its optical axis. This type of stream double refraction, where it is due to the special crystalline structure of the particles, *i.e.*, to their intrinsic double refraction, was called by Freundlich " intrinsic stream double refraction." But there exists another equally important type of case where the colloid units are not themselves doubly refracting, being either amorphous or belonging to the regular crystal system. In this case double refraction can occur if the anisometric particles undergo sufficient parallel orientation and possess a refractive index different from that of the dispersion medium. In the special case of rod-shaped particles the double refraction can then be calculated according to an equation given by O. Wiener.. Freundlich termed this second type of case " morphic stream double refraction." There may exist also morphic dichroism, and cases exist where both intrinsic and morphic optical anistropy occur.

In connection with Freundlich's work on this subject in the field of anisotropic and anisometric particles in colloid sols, it will be remembered that Clerk Maxwell in 1868 investigated the production of " artificial " double refraction by shearing motion in Canada balsam, and that subsequently Kundt (1881), Umlauf (1892), Almy (1897), De Metz (1888—1903) and Hill (1899—1901) published interesting researches on this subject, using a great variety of liquids and producing rotational shear (velocity-gradient) by the relative rotational motion of two concentric cylinders. Almy obtained very curious results in the case of gelatin solutions. The formal mathematical theory based on the strains produced by the shearing stresses and the time of relaxation was dealt with by Maxwell and subsequently by Natanson (1901—1904). The great merit of the work of Freundlich and his collaborators (Diesselhorst, Zocher, Dannenberg) was to demonstrate in the case of certain sols the relation between the " stream " optical anisotropy and the shape (and sometimes the intrinsic optical anisotropy) of the colloid particles in the sols. This work certainly constitutes another of the major contributions of Freundlich to colloid science.

Beginning with a paper published with Seifriz in 1923 on the elasticity of sols and gels, and another with Miss Schalek (in the same year) on the viscosity and elasticity of colloid solutions, Freundlich became deeply interested in the " mechanical," or, as one might now say, the " rheological " properties of colloid systems. The investigations of various cases of anomalous or " structural " viscosity, where the Newtonian viscosity coefficient is no longer constant but decreases with increase of the rate of shear (velocity-gradient), and its time relations (recovery after a period of rest following the motion), prepared him for a famous series of researches on thixotropy, dilatancy, and plasticity. The phenomenon of thioxotropy (a name coined for it by Freundlich) is strikingly shown by a concentrated ferric oxide sol to which a certain amount of electrolyte has been added. The sol sets to a gel or stiff paste which cannot be poured out of the test tube. On vigorous shaking, however, the gel becomes a fairly mobile liquid which can be easily poured, but after a period of rest reverts to the gel state. This reversible isothermal sol $\rightleftharpoons$ gel transformation is a striking (and perhaps rather extreme) example of the general phenomenon of thixotropy. A good account of work on this subject as it stood in 1935 may be found in Freundlich's little monograph on Thixotropy (No. 267 of the *Actualités Scientifiques et Industrielles*, published by Hermann, Paris). The following quotation taken from his last published paper (1942) gives a good summarised account of his latest views.

" It has been found that there may exist a number of intermediate stages between the normal liquid state and the state of a crystalline solid. These are frequently observed in colloidal systems, particularly if they contain a sufficiently high amount of disperse phase. Consequently, concentrated colloidal solutions may differ essentially in their mechanical properties (viscosity, elasticity, etc.) from normal, so-called Newtonian liquids. These differences may be manifold. Two limiting cases are of outstanding importance; the first is that of thixotropy. Whereas the viscosity of a Newtonian liquid is not changed by mechanical means, such as flowing or stirring, a thixotropic system becomes less viscous while flowing or when being stirred. This phenomenon is particularly obvious if we have a thixotropic gel : it is liquefied by shaking and sets again to a gel when at rest. We thus have an isothermal, reversible, sol–gel transformation.

" We are dealing with a thixotropic change, too, if the viscosity of a concentrated sol can be reduced by shaking or stirring and if it increases again when at rest. The viscosity of such a sol differs in other respects from that of a Newtonian liquid. It is anomalous, *i.e.*, it does not obey Poiseuille's law for laminar flow; the amount of liquid passing through a capillary in a given time depends on the applied pressure in a different way. Speaking more specifically, the viscous resistance is not directly proportional to the velocity gradient of the laminar flow, as in Newtonian liquids. The characteristic behaviour of anomalously viscous, thixotropic sols and likewise of thixotropic gels is correlated with the existence of a yield value. This can be demonstrated in a graphic way by using a viscometer, in which a ball is pulled through the viscous system in question by a weight which can be increased at will; for different weights the speed of the moving ball is compared. In a Newtonian liquid the speed is proportional to the weight applied. In a thixotropic sol or gel we have a yield value. The weight must exceed a certain minimum to cause the ball to move; only with higher weights does its speed change in a way similar to that observed in a normal liquid. . . .

" Systems showing anomalous viscosity also exhibit a characteristic behaviour with respect to their electrical conductivity. The electrical conductivity of an aqueous solution is markedly influenced by its Newtonian viscosity; as a rule, it is, in a first approximation, inversely proportional to the viscosity. For instance, the electrical conductivity of an aqueous salt solution having a fairly high viscosity, owing to the

presence of a suitable concentration of glycerol, is lower than that of a solution of the same salt concentration in pure water. The anomalous viscosity of a thixotropic sol or gel, on the other hand, leaves the electrical conductivity practically unchanged. The electrical conductivity of a salt solution remains the same, although it may contain so much gelatin that its apparent viscosity is about equal to that of the solution containing glycerol. It is well known that even gels of gelatin (containing electrolytes) or of soaps do not differ in their electrical conductivity from the sols from which they were produced. Presumably the movement of the ions is not influenced by the structure of thixotropic sols and gels, which is very coarse compared to the small size of the ions.

" Finally, not only gels but also sols of this type (gelatin, soaps, etc.) show elastic properties. Small solid particles suspended in such a sol may be moved by an external force but return to their original position when the force stops acting, a phenomenon not observed in Newtonian liquids. This elasticity in sols is not found so regularly as the other characteristic properties just mentioned. The presence of distinctly rod-shaped colloidal particles is perhaps more decisive in causing elastic effects than it is with the other properties characteristic of this kind of anomalous viscosity.

" Thixotropic behaviour is not exceptional; it is very common, provided that suitable concentrations of the colloid are chosen. Examples are: thixotropic, aqueous gels of many oxides (aluminium, iron, scandium, vanadium, titanium, thorium, etc.), of colloidal bentonite, of myosin, and tobacco mosaic virus, of dibenzoyl-cystine and of barium malonate in a medium of water and alcohol. Aqueous solutions of gelatin have been found to show thixotropy, both as concentrated solutions and as gels.

" Coarse suspensions containing particles with a diameter of 1 μ and more may also be thixotropic. They behave as a liquid while being shaken and settle to a solid paste when shaking stops. This behaviour is again found very frequently with aqueous suspensions of clays, slates (Solnhofen slate), and many powdered minerals (mica, iron oxide, jet, etc.); with finely powdered mercaptobenzothiazole in many organic liquids (light petroleum, carbon tetrachloride, chloroform, benzene, toluene, etc.); and in suspensions of many pigments in oils. Bentonite is a particularly good example of a substance forming thixotropic systems both in colloidal and in coarse suspensions. The mechanical properties of coarse suspensions are important because they enable us to understand better the mechanism of these phenomena. Hence I shall have to refer to them frequently, although protoplasm is certainly a truly colloidal system containing very much smaller particles.

" The other limiting case is that of dilatancy. So far, it has been investigated only in coarse suspensions. Although observed and named by Osborne Reynolds in 1885, it has only recently been recognised as a remarkable counterpart to thixotropy. Osborne Reynolds used the term when describing the behaviour of moist quartz sand: It whitens and appears to be dry when the foot falls on it and becomes wet again when the foot is raised. An aqueous suspension of finely ground quartz powder (particle size 1 to 5 μ) at a concentration of about 44% of the solid is strongly dilatant. A glass rod can easily be moved through the mass at low speed, but an enormous resistance is set up if the speed is increased above a certain limit. . . . The suspension behaves like a Newtonian liquid at low speeds but, from a certain higher speed, the behaviour is like that of a solid. Suspensions of intact starch grains in water are strongly dilatant too.

" There is every reason to believe that colloidal solutions may also be dilatant. A colloidal solution of silicic acid of a suitable concentration and p_H is found to be extremely viscous but Newtonian in its behaviour; it becomes hard and brittle, breaking up to a white, dry powder when crushed with a stout glass rod. Left to itself, the powdered mass returns again to its original viscous liquid state. A technical product, Nuodex Calcium-S (a colloidal solution of about 10% calcium naphthenate in a petroleum distillate), shows a similar behaviour.

" The behaviour of coarse particles of suspensions under the microscope gives us a clue concerning that property of the particles which makes a suspension dilatant or thixotropic. The particles of a dilatant suspension are quite independent of each other; there is not the least indication of coagulation. If they are settled on the slide, they are all separated from each other; if dislodged and driven into the liquid by a slight knock, they remain separated in Brownian movement until they have settled again. On the other hand, the particles of a thixotropic suspension are always found to be coagulated to a certain degree, sticking together and forming clusters. If brought into suspension in the liquid, they may be temporarily separated from each other, but they always unite again to clusters.

" This distinctive behaviour allows us to understand many results obtained with thixotropic or dilatant systems. For instance, in order to make a concentrated iron oxide sol thixotropic a small amount of a coagulating electrolyte like sodium chloride must be added, an amount much smaller than that needed for actual coagulation. In agreement with the positive zeta-potential of the iron oxide particles and with the Schulze–Hardy rule, the anions are especially effective. Smaller concentrations of multivalent anions are necessary to obtain the same state of thixotropy, which is characterised by the same time of re-solidification to a gel after the original gel has been liquefied to a sol by shaking. The thixotropic state, therefore, is often considered to be a primary stage of coagulation.

" The following experiments done by W. Heller prove this concept more quantitatively. If an iron oxide sol, which is just too dilute in iron oxide to give a thixotropic gel on adding a certain amount of electrolyte, is centrifuged after the electrolyte has been added, a more concentrated, gelatinous sediment is accumulated at the bottom of the vessel. This sediment is not formed on using the same centrifugal force, if no electrolyte has been added. The sediment can be reversibly redispersed in the liquid by shaking. If the sediment is separated

from the less concentrated liquid on top, it is found to be a normal, *i.e.*, reversible, thixotropic gel. From the way the rate of sedimentation is correlated with the concentration of the added electrolyte, it can be concluded that reversible coagulates are formed. These are very rich in water and contain a number of colloidal iron oxide particles. This number increases greatly with increasing concentration of the added electrolyte. Such reversible coagulates, " geloids," are also formed in the original dilute sol on adding electrolyte, but their concentration is not high enough to let them coalesce to a coherent structure and turn the whole sol to a gel. If, however, the geloids are concentrated by centrifuging, they coalesce to a thixotropic gel. By investigating the change of so-called conservative light absorption during the process of thixotropic gelation, *i.e.*, the light absorption caused exclusively by the scattering of light (due to the presence of the colloidal particles), it can be shown that the reversible coagulation causing thixotropy is always accompanied by a certain degree of irreversible coagulation, which increases strongly with increasing electrolyte concentration. This irreversible coagulation is the chief factor in the regular coagulation occurring at higher concentrations of electrolyte.

" How many colloidal particles are contained in a geloid and how their number depends on the nature of the colloid is not known. These differences may be marked, as can be concluded from the fact that the minimum concentrations of colloid, when a thixotropic gel is formed, vary distinctly : for an iron oxide sol (of the Graham type), this concentration is about 5 g. per litre, for a vanadium pentoxide sol, it is only about 0·1 g. per litre.

" Thixotropy may be sensitive to very small changes in the concentration of substances contained in the sol. Thus iron oxide sols are particularly sensitive to hydrogen and hydroxyl ions; the time of solidification is strongly increased by an increase in hydrogen ions, decreased by an increase in hydroxyl ions, *i.e.*, an increase in hydrogen ions has a liquefying effect and vice versa. A p_H change from 3·9 to 3·1 caused the time of solidification to rise from 82 seconds to 150 minutes. By dipping a silver plate into an iron oxide gel for 18 hours, the p_H changed from 3·4 to 3·8, producing a decrease in the time of solidification from 33 minutes to 72 seconds. It was further found that amino-acids had a liquefying action upon these gels, independent of the change they caused in p_H, *i.e.*, they increased the time of solidification, although they increased the p_H.

" It is important also from a biological point of view, that not only electrolytes, but also suitable organic non-electrolytes, are able to produce thixotropy. Alcohol added to a suitable iron oxide sol makes it thixotropic. We are probably dealing with a coagulation due to " dehydration." These iron oxide sols may be considered to be sufficiently hydrophilic to allow one to expect such effects of dehydration as are discussed by Kruyt and Bungenberg de Jong in their theory of the stability of hydrophilic sols and of coacervation. If the alcohol is removed from the thixotropic gel by exposing it to sulphuric acid in a desiccator, the gel is liquefied to a sol.

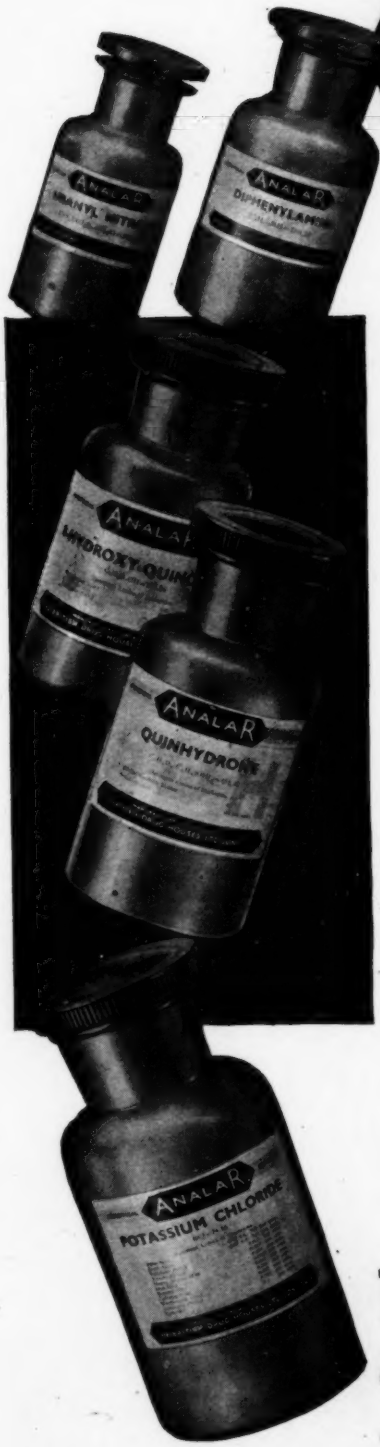
" All these results show that substances causing a certain degree of coagulation lead to the formation of thixotropic systems. Inversely, a strong peptising agent, making the particles independent of each other, can transform a thixotropic system (having the proper particle size) into a dilatant one. A technical dispersing agent, " Hornkem," a sulphonated product of vegetable origin, applied in a suitably high concentration in aqueous solution, acts upon zinc oxide particles in such a way that it produces a strongly dilatant suspension, parallel with a maximum degree of dispersion. In pure water, the same zinc oxide produces a very stiff paste without any indication of dilatancy. In this case it can even be observed that thixotropy requires a medium degree of coagulation : in pure water the degree of clustering is too great to allow a thixotropic behaviour of the suspension; if, however, the right amount of a dilute solution of Hornkem is added, the paste becomes thixotropic, whereas at higher concentrations of Hornkem a state of high dispersion and dilatancy is reached.

" It fits in well with these results that a dilatant paste can be transformed into a thixotropic one by causing a certain degree of coagulation of the particles. Hydrophilic colloids at low concentrations favour the coagulation of hydrophobic particles, the phenomenon of sensitisation; whereas at high concentration they protect the hydrophobic system. In this way lecithin at low concentrations may coagulate aqueous quartz suspensions to a certain degree; this is proved by the marked increase in the rate of sedimentation of the clustered particles after lecithin has been added. Only in this range of sensitisation by the lecithin are these quartz suspensions found to be thixotropic, whereas they are dilatant in pure water.

The following facts cannot, presumably, be applied to biological phenomena, but they deserve to be mentioned briefly, nevertheless. The thixotropic or dilatant state depends strongly on the dispersion medium. Whereas suspensions of quartz or of intact starch grains are dilatant in water, they are thixotropic in organic liquids such as benzene, carbon tetrachloride, etc. It is possible to pass gradually from one state to the other by using two miscible liquids.

" In these organic liquids, too, a small amount of a second substance may cause a marked change in behaviour. A paste made from a very fine iron powder and carbon tetrachloride is pronouncedly plastic, a behaviour which is practically always correlated with a marked thixotropy. On adding a small amount of oleic acid, the paste is liquefied to a strongly dilatant suspension. The adsorption of the oleic acid on the surface of the particles produces a state of independence, and hence dilatancy.

" Suspensions of finely powdered solids in organic liquids, such as mixtures of oils, have been used for a very long time as paints. It is therefore no wonder that painters have been acquainted with the manifold, anomalous mechanical properties of suspensions, though without having defined such limiting cases as thixotropy and dilatancy. But it can hardly be doubted that many pastes of paints, described as stiff and plastic and as having a marked yield value, are thixotropic (in our terminology) if the concentration of the solid is suitably chosen, whereas if they were dispersed to a mobile liquid by the right dispersing agent, they would show dilatancy,



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